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INFLUENCE OF Cr-ATOMS ON THE MAGNETIC AND ELECTRICAL PROPERTIES IN $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ COMPOUNDS*

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AC magnetic susceptibility, electrical resistivity and X-ray Photoelectron Spectroscopy (XPS) measurements have been performed on the $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds with $x = 0.0$, 0.03, 0.05, 0.10, 0.15 and 0.20. A strengthening of the $\mathrm{HoCo_2}$ ferrimagnetism shows up through a rapid increase at small Cr concentration x of the Curie temperature T_{C} which reaches a maximum around $x = 0.15$. The lattice parameters also go through a maximum for the same concentration of Cr. A remarkable decrease of the density of states near the Fermi level is observed for the sample with $x = 0.20$. We correlate the changes of the Curie temperature with the decrease of d-electron concentration when Cr substitutes for Co.

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1. Introduction

The intermetallic compounds $\mathrm{RCo_2}$ with the cubic Laves phase structure show interesting magnetic properties and they are very suitable to study the nature of $3d$ and $4f$ magnetism [1–3]. The magnetic structure in the ground state is ferrimagnetic, it means that the magnetic moments of Co atoms align in antiparallel to those of R atoms [4]. Co magnetism may be formed through a meta-magnetic transition with an external magnetic field [5–7] or by employing the large molecular field due to ferromagnetically ordered $4f$ moments in the magnetic rare-earth-$\mathrm{Co_2}$ compounds [8]. As a consequence, the magnetic phase transition of the first-order type was observed for the compounds with R=Dy, Ho, Er and Tm, but it was of the second-order for R=Gd and Tb.

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Co-magnetism can also be induced in RCo_2 with increasing the density of state at the Fermi level $N(E_F)$. The nature of increasing $N(E_F)$ may be attributed to the volume effects or the effects of the decrease of the d-electron concentration [9]. The substitution of Co by other atoms is a very effective way in producing these effects. In the case of replacement of Co by Al and Mn atoms in $R(Co_{1-x}Al_x)_2$ and $R(Co_{1-x}Mn_x)_2$ compounds a giant increase of T_C was observed [10,11]. The common feature in these systems is that T_C increases at small amounts of substitutions and passes over a maximum at the same dilutant concentration x for all R ($x = 0.12$ and 0.25 for Al and Mn systems, respectively). Upon the substitution also the first-order transition of $HoCo_2$, $DyCo_2$ and $ErCo_2$ has been changed to the second-order. The $R(Co_{1-x}Fe_x)_2$ systems usually show a maximum in T_C and in the $3d$ moment at high Fe content [12]. A strong enhancement of the ordering temperature was observed in the $R(Co_{1-x}Si)_2$ compounds with Ho and Er in the conditions of invariable-crystal-unit-cell-parameter [13–15]. The changes of the magnetic parameters and also the electrical resistivity behaviour observed in the most of investigated $R(Co_{1-x}M_x)_2$ compounds (M=nonmagnetic or magnetic element) were discussed in terms of changes of the electronic structure and their influence on the hierarchy of exchange interactions and formation of the Co moment in this class of materials.

In this work we present the results of the magnetic, electrical and the electronic structure investigations for $Ho(Co_{1-x}Cr_x)_2$ system with $x = 0.0$, 0.03, 0.05, 0.10, 0.15, and 0.20. Chromium has two $3d$ electrons less than cobaltium and posses a similar electronic structure as manganium, so is a good candidate to investigate the role of the substitution atoms at the Co sites.

2. Experiments

Polycrystalline samples of the $Ho(Co_{1-x}Cr_x)_2$ pseudobinary compounds, with $x = 0.0$, 0.03, 0.05, 0.10, 0.15 and 0.20 were prepared by arc melting constituent metals under an argon atmosphere. In order to prevent the samples from foreign impurities, the initial stoichiometry of components was chosen as $Ho(Co_{1-x}Cr_x)_{1.8}$. The ingots were remelted several times and after that annealed in quartz tubes at 720°C for 7 days.

Phase identification of the alloys was performed by X-ray diffractometry Simens D5000. All samples exhibited a single cubic Laves phase of the $MgCu_2$ type, no other phase has been identified. The investigations of the compounds have been performed using the following methods:

- AC-susceptibility measurements were carried out at frequency of 1kHz in the temperature range 77°–300° K. For $HoCo_2$ compound the measurement was performed between 4.2°–300° K.

- DC-susceptibility measurements were done using the Faraday method in an applied magnetic field of 0.25T in the temperature range 77°–300° K.

- The electrical resistivity $\rho(T)$ was measured quasi-continuously at a slowly changing temperature (4.2°–300° K) by a standard four-probe technique. The dimensions of the sample were close to $1\times1\times5$ mm^3.

- The electronic structure of the samples was studied with the use of X-ray Photoelectron Spectroscopy (XPS). The XPS spectra were obtained with monochromatised AlK_α radiation ($\omega = 1486.6$ eV) at room temperature using a PHI 5700/660 Physical Electronics Spectrometer. The energy spectra were analysed with a hemispherical mirror analyser with the energy resolution of 0.3 eV. All emission spectra were measured immediately after breaking a sample in vacuum of 6×10^{-10} Torr. The breaking in high vacuum produced clean surfaces, free of oxygen and carbon contamination.

3. Results and discussion

In Fig. 1(a) we can see the AC susceptibility data of the $Ho(Co_{1-x}Cr_x)_2$ compounds as a plot of reduced $\chi/\chi_{\rm max}$ *versus* temperature T, where $\chi_{\rm max}$ is the highest maximum value of χ. For the sample with $x = 0.0$, for which compound the para-ferrimagnetic transition is of the first order, $\chi_{\rm AC}(T)$ curve is characterised by a double peak (Fig. 1(b)). With increasing Cr concentration from $x = 0.0$ to $x = 0.03$ the increase of Curie temperature $T_{\rm C}$ of about 20 K is observed. In the range of x between 0.03 and 0.10, $T_{\rm C}$ is almost constant and after that passes over a maximum at the concentration $x = 0.15$ and decreases at $x = 0.20$. The Curie temperatures obtained from AC measurements are presented in Fig. 2. The difference between the Curie temperature of $HoCo_2$ and $Ho(Co_{0.85}Cr_{0.15})_2$ compounds was found as 60 K, however this increase is only about half of that observed in $Ho(Co_{1-x}Mn_x)_2$ compounds [11]. The concentration dependence of the lattice parameter $a(x)$ for $Ho(Co_{1-x}Cr_x)_2$ system is also shown in Fig. 2. It is seen that with the substitution of Co by Cr, a increases at first, then reaches a maximum at $x = 0.15$ and decreases for $x = 0.20$.

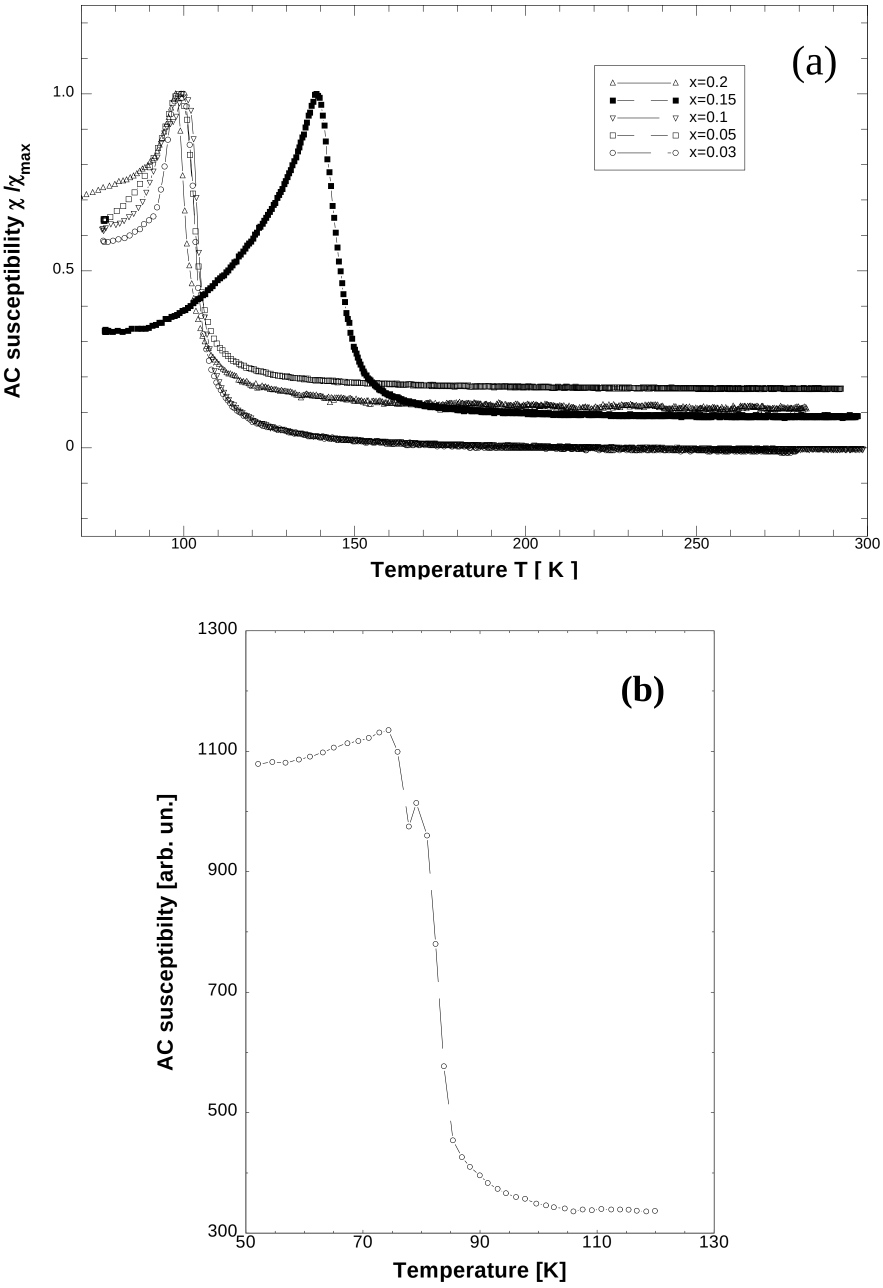

Fig. 1. (a) AC susceptibility $\chi/\chi_{\max}$ *versus* temperature for $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds. (b) AC susceptibility *versus* temperature for $\mathrm{HoCo_2}$ compound.

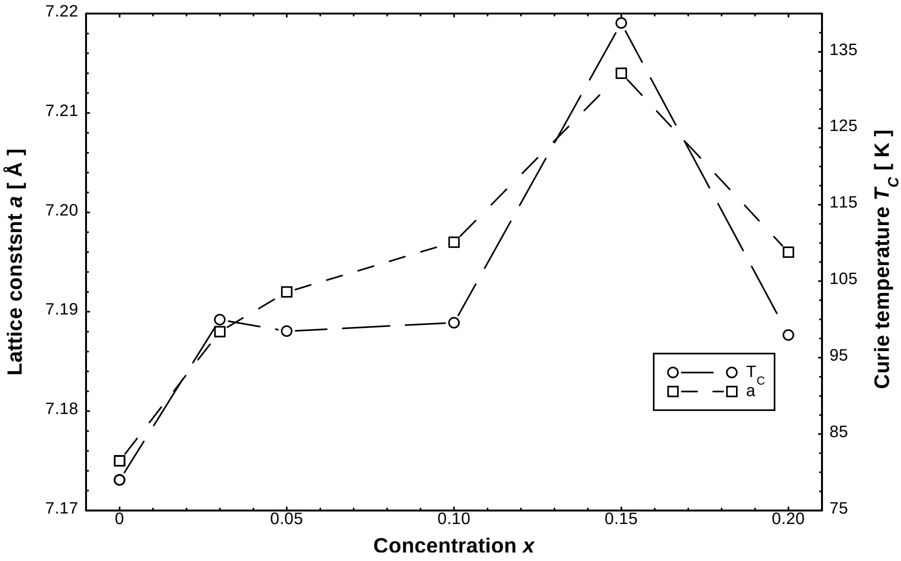

Fig. 2. Lattice constant a and Curie temperature T_C *versus* concentration x for $\mathrm{Ho(Co_{1-x}Cr_x)_2}$.

In Fig. 3 we present data on the temperature dependence of the electrical resistivity $\rho(T)$ of the $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds. For all samples, the electrical resistivity tends to saturate above T_C. In the $\mathrm{HoCo_2}$ the first order transition shows up in the almost discontinuous change in the resistivity

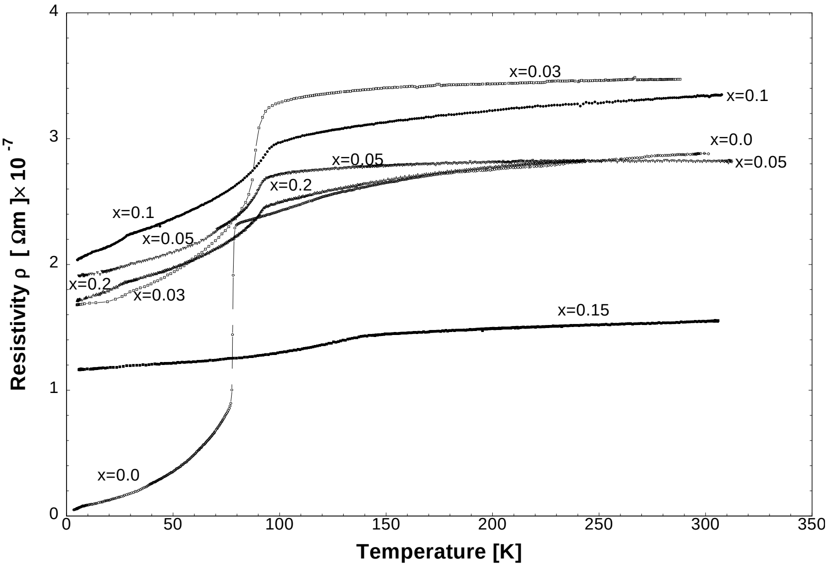

Fig. 3. Electrical resistivity ρ *versus* temperature for $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds.

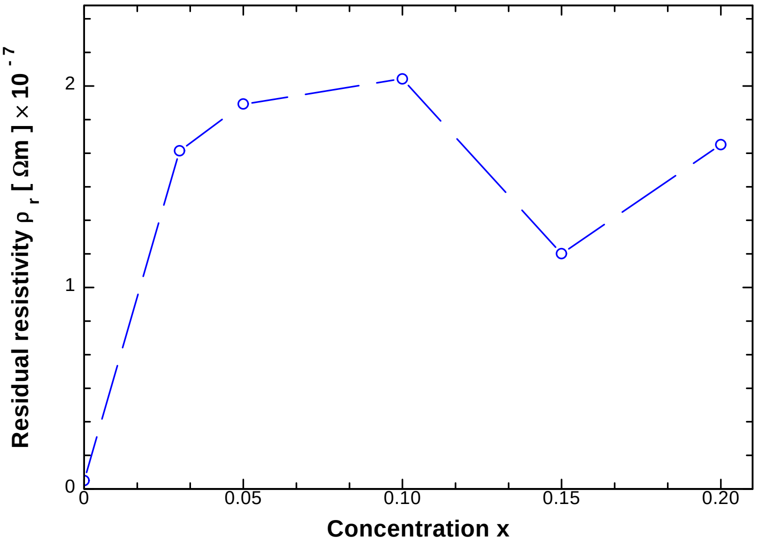

Fig. 4. Residual resistivity ρ_r *versus* concentration x for $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds.

at T_C. In the samples with $x > 0.0$ the resistivity shows no discontinuity at all. With substitution of Co by Cr the value of the residual resistivity ρ_r increases sharply at $x = 0.03$, further increase of Cr concentration makes no significant effect on ρ_r (Fig. 4). The increase of the ρ_r value points to a certain degree of substitutional disorder in the Co/Cr sublattice.

The temperature dependence of the magnetization of the $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds shows the highest value of the magnetization at the concentration $x = 0.15$. It can be concluded that the increase of T_C is connected, besides the lattice expansion effects, with the increase of the magnetization of the d-subsystem, leading in turn to the increase of the f–d exchange interaction. Such a behaviour of magnetization was observed in the $\mathrm{Ho(Co_{1-x}Mn_{1-x})_2}$ [11] and $\mathrm{Ho(Co_{1-x}Si_x)_2}$ [15] systems.

The XPS spectra for valence band region of the $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds ($x = 0.0$, 0.10, 0.15 and 0.20) are presented in Fig. 5(a). We do not observe any change in the position of the $4f$ peak of Ho with the replacing Co by Cr. The bands of width of an order of 2 eV near the Fermi level ($E_\mathrm{F} = 0$) show dominating Co $3d$ states hybridised with Cr $3d$ and Ho $5d$ states (Fig. 5(b)). The influence of Co substitution by Cr atoms on the shape of the bands is small for the concentration $x = 0.10$ and 0.15, but is pronounced when $x = 0.20$.

Summarising, we have demonstrated in this investigation that magnetic and electric properties of $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds are very sensitive to the Co/Cr substitution. The first-order transition in $\mathrm{HoCo_2}$ changes to

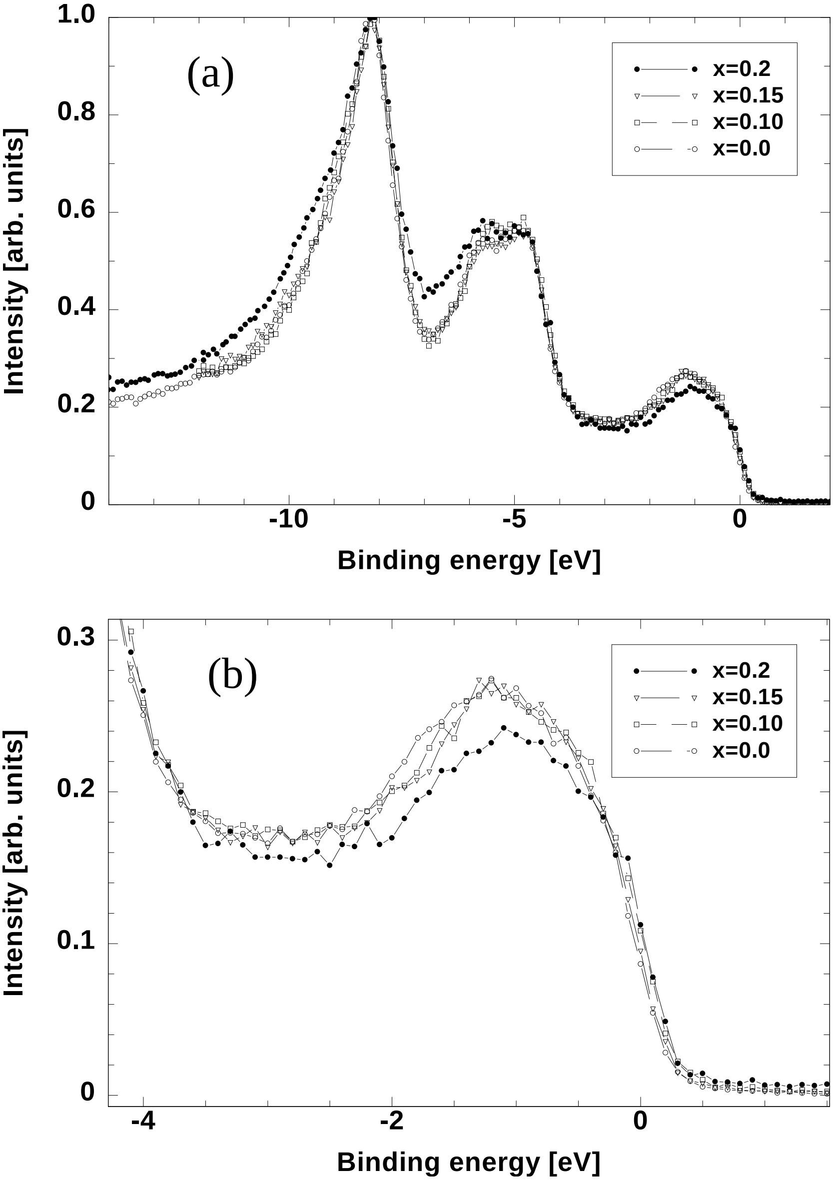

Fig. 5. (a) XPS-valence band region of $\mathrm{Ho(Co_{1-x}Cr_x)_2}$ compounds. (b) XPS-valence band region near the Fermi level for $\mathrm{Ho(Co_{1-x}Cr_x)_2}$.

second-order when the small amount of Co replace with Cr atoms. Compared to the $\mathrm{R(Co_{1-x}Mn_x)_2}$ and $\mathrm{R(Co_{1-x}Al_x)_2}$ systems, the effects of $3d$-electron concentration in the investigated compounds are similar, namely the giant increase of the Curie temperature is observed. Moreover, the Curie temperature $T_\mathrm{C}(x)$ and the lattice parameter $a(x)$ go trough a maximum in the same range of x. We consider the effects of Cr-substitution as caused partly by the lattice expansion, but also by the decrease of d-electron concentration, which leads to the modification of the magnetic behaviour.

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