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Ferromagnetic Order in Single-Crystalline $(Cd_xAl_y)[Cr_2]Se_z$ Semiconductors

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Measurements of the magnetic properties, the electrical conductivity and the Seebeck effect were performed on single crystals $(Cd_xAl_y)[Cr_2]Se_z$ between 77 and 300 K. All samples have a ferromagnetic order with the Curie temperature of 130 K and the paramagnetic Curie–Weiss temperature of 155 K. Both these temperatures do not depend significantly on the Al substitution. The electrical conductivity of single crystals $CdCr_2Se_4$ doped with Al was p-type and showed the change of $\log\sigma$ versus $1/T$ slope above 150 K. This fact is interpreted as being due to the onset of impurity conduction and structural defects.

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1. Introduction

Ferromagnetism has been found in several ternary chromium compounds crystallizing in spinel structure [1, 2]. These compounds are both semiconducting and ferromagnetic with relatively high Curie temperature. Pure $CdCr_2Se_4$ combines p-type semiconducting and ferromagnetic properties with the Curie temperature $T_C = 142$ K and the Curie–Weiss temperature $\theta_{CW} = 190$ K [1]. In literature some reports appeared on the properties mentioned above, in particular an anomalous temperature dependence of the electrical conductivity of In-doped and Ga-doped n-type $CdCr_2Se_4$ [2–4]. Newer reports concern isostructural single-crystalline $CdCr_2Se_4$ spinel systems doped with In [5], Sb [5–7] and Ga [8, 9] as well as polycrystalline $Cd_xCr_yV_zSe_4$ spinel series [10]. They are ferromagnets and p-type semiconductors for small In, Sb, Ga and V content. For higher content antiferromagnetic order, spin-glass and n-type conduction occur.

This paper reports the electrical and magnetic properties of $CdCr_2Se_4$ single crystals doped with Al in the compositional range of Al up to $y = 0.04$.

2. Experimental details

New nonstoichiometric single crystals of $(Cd_xAl_y)[Cr_2]Se_z$ (where $0.02 \leq y \leq 0.04$) were prepared using a chemical vapour transport method. As the starting materials, binary selenides (CdSe, Al_2Se_3) and anhydrous chromium chloride ($CrCl_3$) were used. The chemical composition of the $(Cd_xAl_y)[Cr_2]Se_z$ single crystals were determined using an electron microscope JEOL (7600F) with a microprobe EDS OXFORD. Good quality samples of the $(Cd_xAl_y)[Cr_2]Se_z$ spinel series were selected under a stereoscopic microscope. The structure refinements of the spinels under study were done using a KM 4-circle diffractometer (Kuma Diffraction) and a SHELXL-93 computer program [11]. The single crystals under study crystallize in the cubic system with the space group $Fd\bar{3}m$ (No. 227). Two diamagnetic ions, Cd and Al, differing in ionic radii and charge ($r_{Cd2+} = 78$ and $r_{Al3+} = 39$ pm [12]), occupy tetrahedral 8a positions, while the magnetic Cr ions are in the octahedral 16e sites. Refinement of the site occupation factors (SOFs) revealed a certain amount of the Se deficit in the anion 32e sites (Table I).

The electrical conductivity has been measured with the four-probe dc method using the apparatus with Keithley K181 digital multimeters. The thermoelectric power was measured with a differential method using the temperature difference ΔT of about 2 K. The electrical and thermal contacts between the single crystal and the copper rods were maintained with a silver lacquer mixture (Degussa Leitsilber 200). The thermoelectric power and the electrical conductivity of the same sample were measured along the $\langle 001\rangle$ direction. The crystal orientation about the $\langle 001\rangle$ crystallographic zone axis was based on 12–18 centred X-ray diffraction reflections with the Bragg angles in the range $107^\circ \leq 2\theta \leq 144^\circ$ (Mo K_α radiation). The crystal data are summarized in Table I. The electrical measurements in the $\langle 111\rangle$ direction, performed for comparison, showed unimportant difference with those along $\langle 001\rangle$. Ac and dc magnetization and magnetic susceptibility were measured using a Quantum Design System (MPMS XL) at magnetic field up to 70 kOe and in the temperature range 4.2–300 K.

3. Results and discussion

Magnetic and electrical measurements carried out on the $(Cd_xAl_y)[Cr_2]Se_z$ single crystals are presented in Table II and Figs. 1–3. They revealed a ferromagnetic order with a Curie temperature $T_C \approx 130$ K and a paramagnetic Curie–Weiss temperature $\theta_{CW} \approx 155$ K as well as a p-type conduction. T_C and θ_{CW} do not significantly depend on the Al substitution. The effective magnetic moment slightly decreases from 6.40 μ_B/f.u. for $y = 0.02$

TABLE I

Chemical composition, crystal data, structure refinements, atomic positions, selected distances and angles for $(Cd_xAl_y)[Cr_2]Se_z$ spinel system. a and u are the lattice and anion positional parameters, respectively, d is the calculated density, R_1 and wR_2 are the final factors.

Chemical composition			
x	0.98	0.97	0.96
y	0.02	0.03	0.04
z	3.95	3.93	3.88
Crystal system: cubic; space group: $Fd\bar{3}m$			
Crystal data			
a [pm]	1074.39(2)	1074.28(2)	1073.82(2)
u	0.26431(1)	0.26431(1)	0.26428(1)
d [Mg/m^3]	2.55	2.556	2.559
Refinement			
final R_1 [%]	1.68	1.56	1.93
final wR_2 [%]	4.38	3.59	4.41
Site occupation factor (SOF)			
Cd	0.982	0.969	0.958
Al	0.018	0.031	0.042
Cr	1.0	1.0	1.0
Se	0.987 + vac.	0.983 + vac.	0.971 + vac.
Isotropic displacement parameter U_{eq} [$\times 10^3$ Å^2]			
Cd	3.27(4)	1.65(3)	3.04(4)
Al	3.27(4)	1.65(3)	3.04(4)
Cr	2.55(5)	1.20(4)	2.64(5)
Se	2.39(3)	0.92(3)	2.16(3)
Selected interatomic distances in pm			
Cd–Se(2)	259.21(2)	259.11(2)	259.18(2)
Al–Se(1)	254.13(2)	259.11(2)	259.18(2)
Cr–Se(1)	254.19(1)	254.02(1)	254.19(1)
Selected angles in deg			
Se–Cd/Al–Se(4)	109.47(1)	109.47(1)	109.47(1)
Se(3)–Cr–Se(1)	96.71(1)	96.71(1)	97.12(1)
Se(3)–Cr–Se(2)	82.87(1)	82.86(1)	82.88(1)

The atom positions are: (Cd/Al) site: 8a: (1/8, 1/8, 1/8); [Cr] site: 16d: (1/2, 1/2, 1/2); Se site: 32e: (u, u, u).

to 6.06 μ_B/f.u. for $y = 0.4$. The magnetic isotherms measured up to 70 kOe and at 2 K exhibit a saturation magnetization at 2 kOe which remains almost constant as Al content slowly increases.

Below 2 kOe a linear increase in magnetization with increasing magnetic field indicates a lack of spontaneous magnetization. These results suggest the strong ferromagnetic coupling of the magnetic moments both in the (001) planes and between them. One can conclude that in comparison with the $CdCr_2Se_4$ matrix a dilution of magnetic sublattice by the spin defects (Al-ions) weakens both the long and short range ferromagnetic superex-

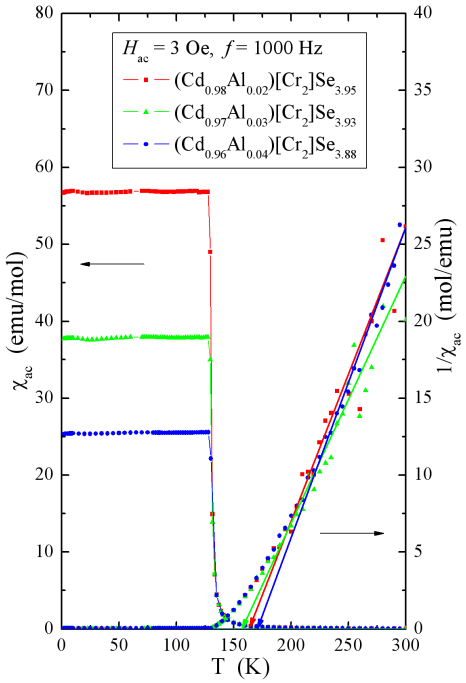

Fig. 1. The ac molar susceptibility χ_{ac} vs. temperature T for single crystals of the $(Cd_xAl_y)[Cr_2]Se_z$ spinel system recorded at $H_{ac} = 3$ Oe, and inverse susceptibility $1/\chi_{ac}$ versus T indicating Curie–Weiss behaviour.

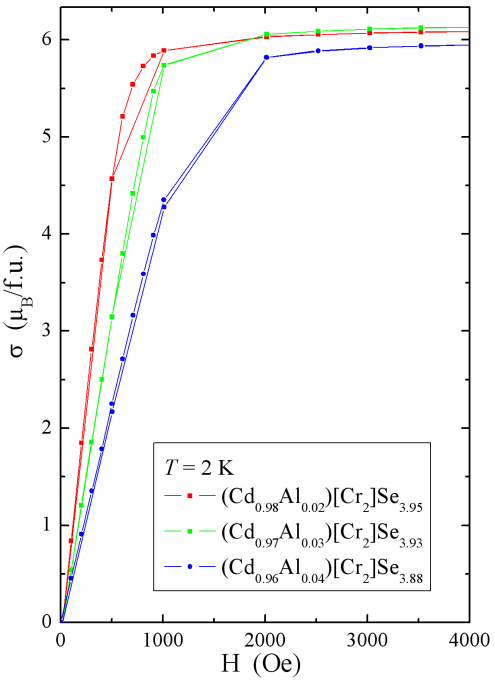

Fig. 2. Magnetization σ vs. magnetic field H recorded at 2 K for $(Cd_xAl_y)[Cr_2]Se_z$.

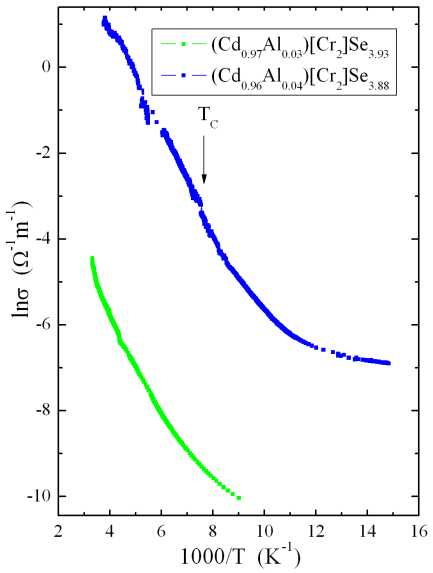

Fig. 3. The electrical conductivity ($\ln\sigma$) vs. reciprocal temperature T^{-1} for $(Cd_xAl_y)[Cr_2]Se_z$.

TABLE II

Electrical and magnetic parameters of the $(Cd_xAl_y)[Cr_2]Se_z$ spinel system. $\mu_{\rm eff}$ is the effective magnetic moment, $C_{\rm M}$ is Curie constant, χ_0 is the temperature independent susceptibility, $T_{\rm C}$ and $\theta_{\rm CW}$ are the Curie and Curie–Weiss temperatures, respectively, σ is the electrical conductivity, $E_{\rm a}$ is the activation energy and S is the thermopower at 300 K.

y	0.02	0.3	0.04
$\mu_{\rm eff}$ [$\mu_{\rm B}$/f.u.]	6.40	6.09	6.06
$C_{\rm M}$ [K/mol]	5.12	4.639	4.59
$\chi_{\rm M}$ [emu/mol]	56.83	37.87	25.53
$T_{\rm C}$ [K]	131.4	130.4	130.1
$\theta_{\rm CW}$ [K]	155.9	150.7	158.8
$\ln\sigma$ [Ω^{-1} m^{-1}]	−4.68	−4.7	1.05
$E_{\rm a}$ [eV]	–	0.1	0.1
S [μV/K]	30	25	120

change interactions in the spinels under study. The Al-substitution strongly affects on the value of the electrical conductivity, but not on the thermal activation, close to 0.1 eV, as well as on the sign of thermopower (see Table II and Fig. 3). A Se non-stoichiometry could change the carrier concentration, too.

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