

Distribution of Metal Ions and Magnetic Properties in Spinel System $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$

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Single crystals of the $\text{Cd}[\text{Cr}_2]\text{Se}_4$ spinel with Ga admixtures were grown by chemical transport with an aim to study the influence of gallium concentration on the cation distribution and magnetic properties of the Cd–Cr–Ga–Se system. X-ray crystal structure determination showed that, unlike the system $\text{Zn–Ga–Cr}_2\text{Se}_4$ in which gallium could accommodate both tetrahedral and octahedral sites, in the compounds under study the Ga^{3+} ions were exclusively substituted for the magnetic Cr^{3+} ions on octahedral sites, while Cd^{2+} ions were located on tetrahedral sites of the cubic close-packed sublattice formed by the selenium ions. The chemical composition of these compounds can be written as $\text{Cd}[\text{Cr}_{2-x}\text{Ga}_x]\text{Se}_4$ ($x = 0, 0.02, 0.04, 0.06, 0.13$). Compared to the parent CdCr_2Se_4 , such a distribution of the cations led to considerably lowered magnetization in saturation states. The ferromagnetic Curie temperature T_C was found to decrease from 129 to 120.2 K, as x varied from 0 to 0.06. The high concentration of Ga^{3+} ($x = 0.13$) caused the paramagnetic Curie–Weiss temperature θ_{C-W} to change the sign to a negative. The nature of the magnetic interactions, developing below $T_N = 214$ K, appeared to be altered from the ferro-to-antiferromagnetic ordering. Thus, this type of doping strongly limits the extent of ferromagnetism in the system Cd–Cr–Ga–Se.

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Key Words: Spinel; chromium selenides; Ga admixture; ferro and antiferromagnetic ordering.

INTRODUCTION

A family of halogenide spinels of the formula $\text{Cd}_{1-x}\text{M}_{2x/3}\text{Cr}_2\text{Se}_4$ ($M = \text{Al}, \text{In}, \text{Ga}$) exhibits magnetic and semiconducting properties (1–6). The ferromagnetic properties of parent CdCr_2Se_4 are a result of dominating interactions between the nearest-neighbor Cr^{3+} ions and of weaker superexchange couplings between the more distant Cr ions (7). Therefore, the observed magnetic moments comprising the values between 5.82 and $5.29 \mu_B/\text{formula unit (f.u.)}$ were

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usually lower than expected, $6 \mu_B/\text{f.u.}$, if the ferromagnetic spin alignment was assumed (1, 8). The Curie temperature reported in literature was in the range 129–142 K, showing the compound to be very sensitive to the methods of preparation and deviations from a stoichiometry (9, 10). This effect was discussed with respect to a deficiency and excess of cations in tetrahedral or octahedral voids of the spinel structure (11). Although there are numerous data available for powder materials, the studies of effect of nonmagnetic Ga admixtures on the single-crystal properties are very few and inconsistent. They raise a question of location of the Ga ions in the tetrahedral or octahedral voids of the spinel structure. It was recently shown that in the system $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$ the Ga^{3+} ions were able to adopt both of these locations, depending on sample stoichiometry and with Zn^{2+} -deficit, gallium-preferred tetrahedral positions (12). There are also some doubts as to the valence of the magnetic Cr^{3+} ($3d^3$) ions since the reduced values of the effective magnetic moments have been explained by the presence of some number of the Cr^{2+} ions that always couple antiparallel to the spins of Cr^{3+} , causing in effect a shift of the paramagnetic Curie–Weiss temperature θ_{C-W} to the lower temperature range (13).

Experimental results reported in the literature so far refer mostly to polycrystalline forms of the ternary selenides. We have prepared a series of Cd–Cr–Ga–Se₄ single crystals with various Ga concentrations for the purpose of studying the influence of the Ga^{3+} admixtures on the cation distribution and magnetic ordering in this spinel system.

EXPERIMENTAL

1. Sample Preparation

Single crystals of the $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$ system were grown by vapor transport in closed quartz ampoules with anhydrous chromium chloride, CrCl_3 , as a transporting agent and with selenides CdSe and Ga_2Se_3 as solid phases (14, 15).

The starting materials, binary selenides, were synthesized from elemental cadmium, gallium, and selenium (purity

99.999%). The stoichiometric mixtures of the elements were pulverized in agate mortar and sealed in evacuated quartz ampoules. After heating at 1075 K for 6 days, the selenides were ground in an agate mortar and an X-ray powder analysis showed that the products contained only the synthesized phase.

The mixture of selenides with CrCl₃ was sealed in quartz tubes (length \sim 200 mm, inner diameter $d = 20$ mm) evacuated to $\sim 10^{-3}$ Pa. These ampoules were heated in a horizontal zone furnace to about 1120 K at the solution zone, maintaining a temperature gradient of 50 K along the ampoule. After 7–10 days, the furnace was cooled to room temperature with the rate 6 K/h.

Single crystals of octahedral shape with well-formed regular (111) faces had the edge lengths of ~ 1 to 3 mm. The chemical composition of the crystals selected for further studies was initially specified by an X-ray microprobe. It

appeared that the Ga concentration was always lesser than that assumed in the chemical synthesis.

2. Single-Crystal X-ray Diffraction

Good quality samples of the system Cd–Cr–Ga–Se₄ with different nominal Ga concentrations have been chosen for single-crystal structure refinements to determine their composition and the exact gallium content. The measurements were performed on a KM-4 diffractometer (Kuma Diffraction). The least-squares calculations of the unit cell dimensions without symmetry constraints and based on 28 to 30 reflections from the range $18.5 \leq 2\theta \leq 34^\circ$ showed the crystals to be cubic. The intensity data for the structure determination were corrected for Lorentz and polarization effects. Prior to structure calculations, the data sets were corrected for absorption using a Gaussian face-indexed

TABLE 1
Summary of the Crystal Data and Experimental Details of the X-ray Structure Refinement

	I	II	III
Crystal data			
Crystal system	cubic	cubic	cubic
Space group	$Fd\bar{3}m$	$Fd\bar{3}m$	$Fd\bar{3}m$
a (Å)	10.741(1)	10.735(1)	10.687(1)
V (Å ³)	1239.2(3)	1237.1(3)	1220.6(3)
Z	8	8	8
Density calc. (Mg/m ³)	5.777	5.782	5.865
Absorption coeff. μ (mm ⁻¹)	31.2	31.3	31.65
Data collection			
Radiation, wavelength (Å)	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
Monochromator	graphite	graphite	graphite
2θ range (°)	6 to 88	6 to 88.3	6 to 110
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan speed (°/s)	0.010 to 0.04	0.010 to 0.06	0.015 to 0.05
Scan width (°)	$1.1 + 0.25 \tan \theta$	$1.15 + 0.25 \tan \theta$	$1.1 + 0.25 \tan \theta$
Index range	$h: -20, 21$ $k: 0, 21$ $l: -20, 20$	0, 18 -18, 0 -20, 20	-23, 0 -23, 21 -13, 23
No. reflections collected	3728	2700	3969
No. independent reflections	272	206	322
No. observed reflections	209	164	163
Standard reflections/measurements	2/50	2/50	2/50
Decay of standards	negligible	negligible	negligible
Refinement			
Refinement on	F^2	F^2	F^2
F_o criterion	$ F_o \geq 2\sigma(F_o)$	$ F_o \geq 2\sigma(F_o)$	$ F_o \geq 2\sigma(F_o)$
Corrections:			
Lorentz polarization			
Absorption (numerical), T_{\min} and T_{\max}	0.45 and 0.62	0.58 and 0.75	0.55 and 0.73
Extinction (empirical as in SHELXL93)	$x = 0.0015(1)$	$x = 0.0055(4)$	$x = 0.0012(1)$
R_{int} (before; after absorption)	0.09; 0.056	0.14, 0.07	0.11, 0.068
Number of varied parameters	10	10	10
Final R_1	0.028	0.024	0.027
Final wR_2	0.081	0.054	0.069
Goodness of fit	1.27	1.08	0.92
Min.; max. residual (e Å ⁻³)	-1.1, 1.4	-1.4, 1.4	-1.7, 1.5

TABLE 2

Structural Characteristics of the Spinel System $(\text{Cd})[\text{Cr}_{2-x}\text{Ga}_x]\text{Se}_4$ for $x = 0.02, 0.06, \text{ and } 0.13$ (The Atomic Positions Are (A) Site $8a, (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$; [B] Site $16d, (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; and Se Site, $32e: x, x, x$ ($= u$ parameter); Thermal Displacement Amplitudes for the Metal Ions Are Given as the Isotropic Temperature Factors U_{iso} and for Selenium as U_{eq})

Sample no. and composition	u parameter	Site occupation		U_{iso} or $U_{\text{eq}} \times 10^3$ (\AA^2)		
		(A)	[B]	at (A)	at [B] site	Se
$(\text{Cd})[\text{Cr}_2]\text{Se}_4^a$	0.265	1.0	2.0			
I: $(\text{Cd})[\text{Cr}_{1.98}\text{Ga}_{0.02}]\text{Se}_4$	0.26419(4)	1.0	1.977:0.023(8)	9.8(3)	6.2(4)	7.2(1)
II: $(\text{Cd})[\text{Cr}_{1.94}\text{Ga}_{0.06}]\text{Se}_4$	0.26417(4)	1.0	1.942:0.058(11)	9.3(2)	6.6(4)	6.1(1)
III: $(\text{Cd})[\text{Cr}_{1.87}\text{Ga}_{0.13}]\text{Se}_4$	0.26350(4)	1.0	1.870:0.130(7)	10.3(2)	7.8(4)	7.5(2)

Note. The anisotropic thermal displacements amplitudes for Se are $U_{ii} = U_{22} = U_{33}$ and their values multiplied by 10^3 (\AA^2) are 7.0(1), 6.1(2), and 7.8(2) in the crystals I, II, and III, respectively; while $U_{12} = U_{13} = U_{23}$ multiplied by 10^4 (\AA^2) are equal to $-5(1)$, $-7(1)$, and $+6(1)$ in the crystals I, II, and III, respectively.

^a After P. J. Wojtowicz, P. K. Baltzer, and M. Robbins, *J. Phys. Chem. Solids* **28**, 2423 (1967).

numerical routine of SHELXL software (14). In Table 1 are given crystal data for three representative samples I, II, and III together with a summary of experimental conditions for the intensity data collection and structure refinements. The structural results for the sample IV were exactly intermediate between those of samples I and II; therefore, they have not been included in Tables 1 and 2.

In all three cases the structure calculations were started with a preliminary model of normal spinel, assuming Cd^{2+} located at tetrahedral A sites and Cr^{3+} at octahedral B sites. Positions of the Ga^{3+} ions were found in the next stage of calculation by considering two separate approaches: one with Ga^{3+} and Cd^{2+} sharing A positions; their individual site occupation factors were varied under constraints of $8a$ site symmetry and the other model with Ga^{3+} coupled together with Cr^{3+} on the $16d$ site symmetry of space group $Fd\bar{3}m$. Upon convergence, the refinement was continued with anisotropic thermal motions of the Se ions. The results of X-ray structure analysis showed that in the samples under study the Ga^{3+} ions were exclusively located on the octahedral sites, substituting Cr^{3+} in proportions denoted in Table 2 as the site occupation factors (SOF). Although charged with relatively large standard deviations, the refined site occupancies enable writing the cation distribution in the crystals I, II, and III as $(\text{Cd})[\text{Cr}_{1.98}\text{Ga}_{0.02}]\text{Se}_4$, $(\text{Cd})[\text{Cr}_{1.94}\text{Ga}_{0.06}]\text{Se}_4$, and $(\text{Cd})[\text{Cr}_{1.87}\text{Ga}_{0.13}]\text{Se}_4$, respectively.

The structures were refined by the full-matrix least-squares method using SHELXL93 program system (16). The origin of the unit cell was taken at the point $\bar{3}m$ of the space group $Fd\bar{3}m$ (No. 227 in the International Tables for X-ray Crystallography). The other results of the refinement are collected in Table 2.

3. Magnetic Measurements

The magnetic measurements were made for single crystals of the system $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$ (with $x = 0, 0.02, 0.04, 0.06,$

and 0.13). The alignment of the cubic samples along the crystallographic axis was not controlled. The magnetic molar susceptibility data were recorded using the Faraday method in the temperature range 77–600 K in a helium atmosphere. A correction subtracting diamagnetic susceptibility for Cd^{2+} , Cr^{3+} , Ga^{3+} , and Se^{2-} has been made using the Slater–Angus method. The Curie temperature was determined by ac susceptibility measurements at a frequency of 1 kHz. The magnetization measurements were carried out in the temperature range 4.2–300 K and in stationary magnetic fields up to 140 kOe.

RESULTS AND DISCUSSION

The single-crystal X-ray diffraction analysis shows that the unit cell dimensions are not very sensitive to the Ga^{3+} content x and they decrease slightly with increasing x . Although small, the volume changes are consistent with the model of the cation distribution resulting from the structure refinement. These structure calculations indicate that Ga^{3+} with the ionic radius $r_{\text{Ga}^{3+}} = 0.62$ shows strong preference to the B sites occupied by Cr^{3+} of comparable size ($r_{\text{Cr}^{3+}} = 0.615$), while the Cd^{2+} ions, having the largest ionic radii among the metals involved ($r_{\text{Cd}^{2+}} = 0.78$), are solely located on the A sites. The relatively large departure of the u parameter (Table 2) from the ideal value 0.250 means that the Se ions moved in the $[111]$ direction away from the nearest tetrahedral Cd ions. No indication of the Cd^{2+} ion deficit has been detected.

The cubic symmetry and isotropic features of the thermal displacement amplitudes of the Se ions suggested that there was no evidence for the Jahn–Teller effect, which could be expected, if a considerable amount of gallium appeared to be located at tetrahedral sites. Such cation distribution induces formation of the Jahn–Teller active Cr^{2+} (d^4) ions, which having the electron configuration $t_{2g}^3 e_g^1$ can produce some amount of distorted octahedra with lower symmetry.

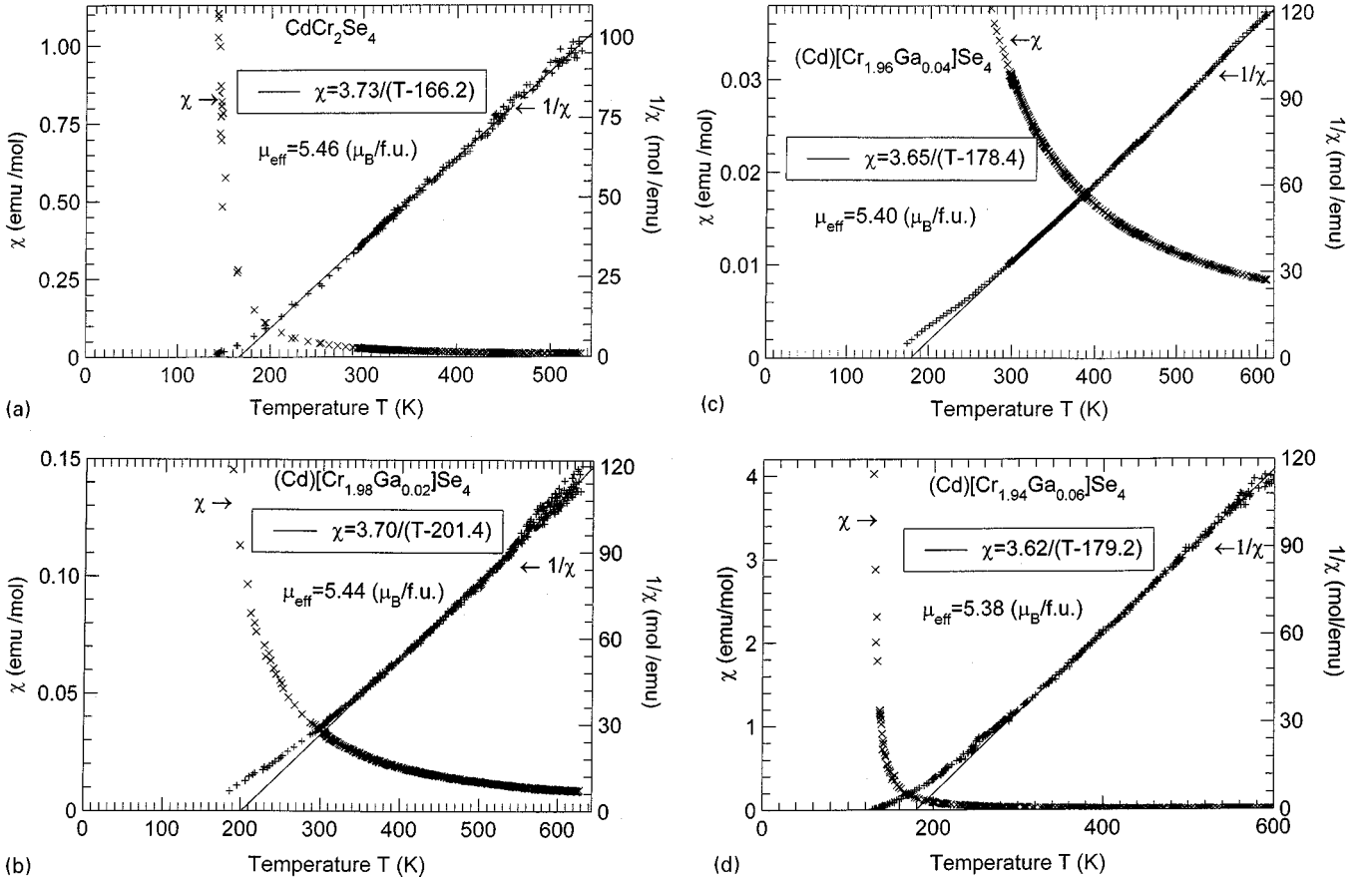


FIG. 1. Temperature dependence of the molar susceptibility χ and its inverse χ^{-1} in (a) parent CdCr_2Se_4 and for the $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$ samples with gallium concentration (b) $x = 0.02$, (c) $x = 0.04$, and (d) $x = 0.06$, respectively.

The resultant static or dynamic Jahn–Teller effect would imply significant anisotropy of the thermal displacements of the Se ions. Even if we can not exclude the presence of some incoherent octahedral distortions in the presented compounds, their ratio was insufficient to be observed.

However, as is demonstrated below, the octahedral location of Ga^{3+} has significant consequences on the magnetic properties.

The temperature dependencies of the molar magnetic susceptibility χ and its inverse χ^{-1} for the single crystals of “pure” CdCr_2Se_4 and for the crystals with $x = 0.02$, 0.04, and 0.06 indicate the ferromagnetic order below T_C (Fig. 1). Above T_C the susceptibility obeys the Curie–Weiss law. The paramagnetic-to-ferromagnetic phase transition temperatures shown in Fig. 2 are lower than $T_C = 129$ K in the parent CdCr_2Se_4 , and they decrease with increasing Ga concentration $x = 0.02$, 0.04, and 0.06. In the sample with high gallium content the magnetic susceptibility and its inverse have quite different runs (Fig. 3), indicating that the ferromagnetic interactions are turned to the antiferromagnetic ordering. This alteration is confirmed by the negative

sign of θ_{C-W} . Table 3 summarizes the results of magnetic measurements.

The paramagnetic Curie temperature θ_{C-W} , which can be a measure of the strength of Cr–Cr interactions leading to the ferromagnetic spin ordering, has a positive sign in the samples with $x \leq 0.06$. It turns out that θ_{C-W} shows a small maximum at low Ga concentration $x = 0.02$ and decreases at the higher Ga content. A similar tendency has been observed in $\text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ (14), but we are unable to pinpoint the reason for this effect.

The present results mean that Ga^{3+} accommodated on the octahedral sites and substituted for Cr^{3+} acted as local defects in the crystal lattice. At low Ga concentration the perturbations in the chromium sublattice destroy some of the paths of ferromagnetic direct interactions between the Cr^{3+} pairs due to an imperfect spin alignment of those Cr ions, which are the nearest neighbors to the Ga admixtures. In nonsubstituted spinel each Cr^{3+} has six equivalent near-neighbor Cr^{3+} ions at the distance $(a/4)2^{1/2}$. The ferromagnetic spin alignment of these near-neighbors will correspond to the theoretical magnetization at the saturation state

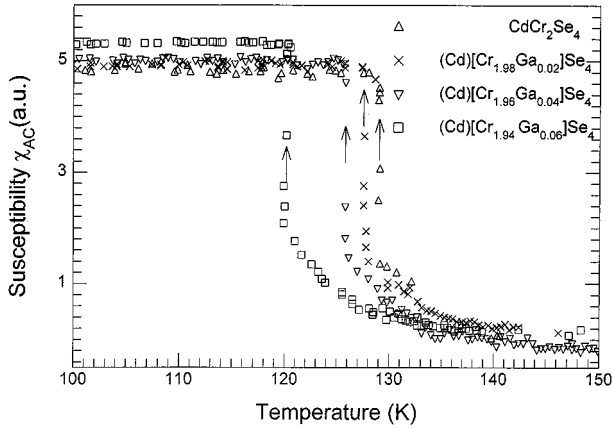


FIG. 2. The ferromagnetic Curie temperature T_C in the system $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$. The arrows show the transition temperatures T_C for the particular compositions.

$\mu_{\text{sat theor}} = 3 \mu_B/\text{Cr}$. In the presence of a Ga^{3+} admixture the value of $\mu_{\text{sat}}/\text{Cr}$ will be reduced by a factor proportional to $6x$, where x is the gallium concentration. The resulting $\mu_{\text{sat}} = \mu_{\text{sat theor}} (1-6x)$ Bohr magnetons/Cr. This simple formula describes quite well the experimental data in Table 3, explaining also the field-dependent magnetization for various Ga contents (Fig. 4). The saturation effects have been observed at relatively low magnetic fields. The higher the Ga concentration, the lower the saturation magnetization for samples with $x = 0.06$ in which the ferromagnetic interactions, competing with antiferromagnetic orderings, are still dominating. The sample with $x = 0.13$ shows antiferromagnetic transition at $T_N = 214$ K (Fig. 3). The magnetization measured in field $H = 140$ kOe and at 4.2 K is very low and far from the saturation.

It appeared thus that Ga admixtures introduced at the Cr sites of these spinels modified their magnetic properties. This type of doping limits strongly the extent of ferromagnetic interactions by hindering the spin exchange process between the nearest-neighbor Cr^{3+} . For samples with high Ga concentration the superexchange mechanism of the type $\text{Cr}^{3+}-\text{Se}-\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}-\text{Se}-\text{Cr}^{4+}$ becomes effective. The

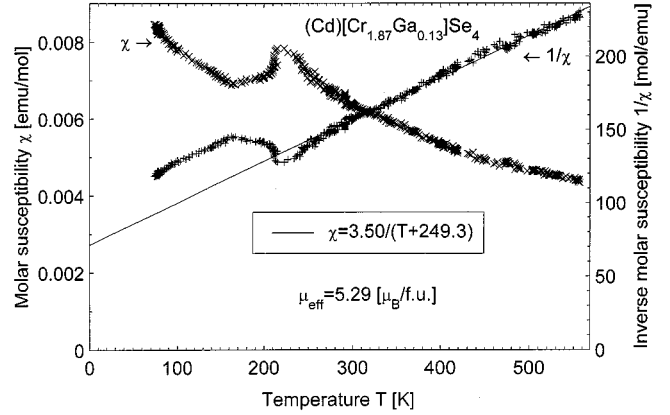


FIG. 3. Temperature dependence of the molar susceptibility χ and its inverse χ^{-1} for the sample with gallium concentration $x = 0.13$.

superexchange interactions between the next-near-neighbors arise from the partly covalent character of the Cr–Se bonding due to the hybridization of the chromium d orbitals and the anionic s and p orbitals (17). A small contribution of the superexchange with antiparallel spin alignment is probably present in the parent sample also, as the molar saturation moments, reported in the literature, are always lower by about $0.5 \mu_B$ from the theoretical value $6 \mu_B$.

CONCLUSIONS

The present study established the influence of the Ga^{3+} dopants on the modification of magnetic properties in the single crystals of the system $\text{CdCr}_{2-x}\text{Ga}_x\text{Se}_4$ ($x = 0.02, 0.04, 0.06,$ and 0.13).

1. X-ray structure analysis for the samples with $x = 0.02, 0.06,$ and 0.13 showed that the crystals are the cubic spinels with normal cation distribution. In all samples under investigation the nonmagnetic Ga^{3+} ions share octahedral positions with the magnetic Cr^{3+} ions. Divalent Cd cations are located solely at tetrahedral positions. The gallium concentration appeared to be lower than that assumed in chemical synthesis.

TABLE 3
Summary of the Magnetic Properties of the System $(\text{Cd})[\text{Cr}_{2-x}\text{Ga}_x]\text{Se}_4$

Composition	$\mu_{\text{eff}} (\mu_B)$		$\theta_{\text{C-W}} (\text{K})$	C_M	$T_C (\text{K})$	$\mu_{\text{sat}} (\mu_B)$ at $T = 4.2 \text{ K}$	
	μ/mol	μ/Cr				μ/mol	μ/Cr
$(\text{Cd})[\text{Cr}_2]\text{Se}_4$	5.46	3.86	166.2	3.73	129.0	5.5	2.75
$(\text{Cd})[\text{Cr}_{1.98}\text{Ga}_{0.02}]\text{Se}_4$	5.44	3.87	201.4	3.70	127.5	4.9	2.47
$(\text{Cd})[\text{Cr}_{1.96}\text{Ga}_{0.04}]\text{Se}_4$	5.40	3.88	178.4	3.65	125.8	4.4	2.24
$(\text{Cd})[\text{Cr}_{1.94}\text{Ga}_{0.06}]\text{Se}_4$	5.38	3.86	179.2	3.62	120.2	3.7	1.91
$(\text{Cd})[\text{Cr}_{1.87}\text{Ga}_{0.13}]\text{Se}_4$	5.29	3.87	-249.3	3.50	$T_N = 214$		

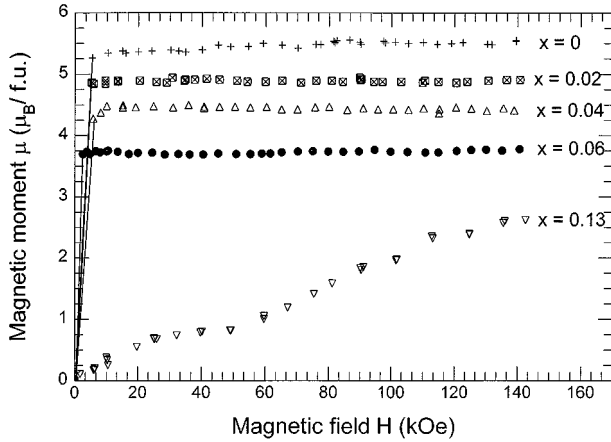


FIG. 4. Magnetization at 4.2 K for the samples with different gallium concentrations ($x = 0.0, 0.02, 0.04, 0.06,$ and 0.13).

2. The effective magnetic moment per one chromium ion is independent of gallium concentration and equal to the theoretical value for the Cr^{3+} ion at the octahedral position ($3.87 \mu_B$). This proves the electronic state of Cr^{3+} in the system of compounds. Admixtures of Ga^{3+} affected strongly the ferromagnetic spin couplings between the Cr^{3+} pairs, reducing the saturation magnetic moments. With the Ga concentration increasing from $x = 0$ to $x = 0.06$, the Curie temperature was lowered from $T_C = 129$ K to $T_C = 120$ K, respectively. High Ga concentration ($x = 0.13$) caused considerable perturbations in the periodicity of the crystal structure, changing in effect the nature of spin couplings from the ferro-to-antiferromagnetic interactions.

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