

Influence of the valence of the substituted cations on the electrical properties of the magnetically modulated spinels $Zn_{1-x} A_x Cr_2 Se_4$ ($A = Cu, Ga_{2/3}$)

T. Groń, H. Duda, and J. Warczewski

Silesian University, Institute of Physics, ul. Uniwersytecka 4, 40 007 Katowice, Poland

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The experimental results concerning the electrical conductivity and the Seebeck effect in the spinel series $Zn_{1-x} A_x Cr_2 Se_4$ ($A = Cu, Ga_{2/3}$) are presented. They serve as a basis for the calculations of both the concentration and the mobility of the current carriers as well as of the Fermi energy in the temperature range of 70–500 K. The results suggest that in the spinel series under study the changes of the electrical conductivity are connected with the changes of both the concentration and the mobility of the current carriers. The strong relation of the magnetic and electrical properties of the spinels under study is emphasized. It turns out that the large electrical conductivity is accompanied here by both the ferromagnetic ordering of the magnetic moments and the partial degeneracy of the semiconductor state, whereas the small electrical conductivity is accompanied here by both the domination of the antiferromagnetic component of the ordering of the magnetic moments and the compensation of the semiconductor state.

I. INTRODUCTION

Much information has appeared in the literature on the magnetic and electrical properties of the spinels with the chemical formulas either $M(Cr_2 X_4)$ or $A_{1-x} B_x (Cr_2 X_4)$, where M , A , and B represent Fe, Zn, Cd, Hg, Cu, or $Ga_{2/3}$ and X represents O, S, Se, or Te. These spinels are either metals or semiconductors, either ferromagnets or antiferromagnets, and finally either ferrimagnets or Pauli paramagnets.

The symbol $Zn_{1-x} A_x Cr_2 Se_4$ represents here a combination of the two spinel series $Zn_{1-x} Cu_x Cr_2 Se_4$ and $Zn_{1-x} Ga_{2x/3} Cr_2 Se_4$ obtained from the spinel $ZnCr_2 Se_4$ by the substitution in place of the divalent Zn of either the monovalent Cu or the trivalent Ga. The structural and magnetic properties of these two spinel series are completely investigated, whereas the electrical properties are only partly explored.

From the crystallographic studies it follows that only the spinel series $Zn_{1-x} Cu_x Cr_2 Se_4$ fulfills Vegard's law in the full-concentration region,¹ whereas the spinel series $Zn_{1-x} Ga_{2x/3} Cr_2 Se_4$ reveals limited solubility.² The fact, that until now the attempts failed to obtain the spinel series $Zn_{1-x} Ga_x Cr_2 Se_4$ and, in particular, the boundary spinel of this series, namely, $GaCr_2 Se_4$, suggests that the configuration of the chromium ions with the mixed valency (Cr^{3+}, Cr^{2+}), which would assure here the electrical neutrality, is not possible. Therefore, statistical substitution of two-thirds of a Ga ion in place of a Zn ion leads to the increase of the imperfection degree of the spinel structure as well as to the break of this structure for $x > 0.6$. The multiphase structure of $Zn_{1-x} Ga_{2x/3} Cr_2 Se_4$ for $x > 0.6$ confirms the above considerations.² From the studies of magnetic properties it follows that the spinels of the series $Zn_{1-x} A_x Cr_2 Se_4$ reveal a variety of the magnetic structures.^{3,4} One observes (see Fig. 1) the simple spiral for $0.5 (Ga_{2/3}) \leq x \leq 0.025$

(Cu), the ferromagnetic spiral for both $0.05 (Cu) \leq x \leq 0.1 (Cu)$ and $0.2 (Cu) \leq x \leq 0.7 (Cu)$, and the ferromagnetic ordering for $x \geq 0.8 (Cu)$. Moreover, the neutron-diffraction studies carried out on the spinel $Zn_{0.89} Cu_{0.11} Cr_2 Se_4$ suggest the existence of the magnetic cluster glass for x somewhere between 0.1 (Cu) and 0.2 (Cu).⁵ From the studies of magnetic properties it follows also that in the spinel series $Zn_{1-x} Cu_x Cr_2 Se_4$ the mixed valency of Cr ions (Cr^{3+}, Cr^{4+}) (Ref. 3) occurs and the double exchange magnetic interaction dominates, especially acting strongly above the percolation threshold (i.e., $x = 0.2$). In the spinel series $Zn_{1-x} Ga_{2x/3} Cr_2 Se_4$ the superexchange magnetic interaction dominates, in principle, and the suggestions concerning the mixed valency of the Cr ions (Cr^{3+}, Cr^{2+}) in this series⁴ seem to be wrong in the light of the crystallographic² and EPR (Ref. 6) investigations.

The investigations of the electrical properties of the series $Zn_{1-x} A_x Cr_2 Se_4$ carried out up to the present are limited to the boundary spinels, i.e., either with $x = 0$ or

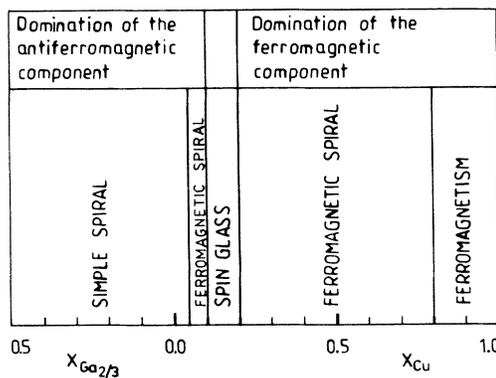


FIG. 1. Magnetic structures in $Zn_{1-x} A_x Cr_2 Se_4$.

with $x=1$ (for the spinels with Cu) as well as for the spinels with small x . It was found that the spinel CuCr_2Se_4 is characterized by the p -type metallic conductivity^{7,8} and the spinel ZnCr_2Se_4 is a p -type semiconductor.⁶⁻⁸

The investigations of the electrical resistivity carried out on the single crystal of ZnCr_2Se_4 in different crystallographic directions⁹ show the temperature independence of the electrical resistivity at low temperatures and its dependence on the crystallographic direction. The studies of magnetoresistance carried out on the same single crystal at the magnetic field of 0.715 T show its large negative values (~ -0.2) with the minimum near the Néel temperature (~ 20 K) and quickly coming to zero in the temperature range of 20–110 K. The same crystal was also studied with the aid of the synchrotron radiation using the photoelectron spectrometry technique and these investigations suggest a considerable contribution of the covalent bond in the structure of chemical bonds in ZnCr_2Se_4 .¹⁰ Next, the Hall-effect studies of ZnCr_2Se_4 suggest a stronger temperature dependence of the hole concentration than the one of their mobility.⁶ On the other hand, in the spinel ZnCr_2Se_4 doped with 0.24% Cu the hole mobility determined from the Hall effect turned out to be independent of temperature.⁹

The p -type electrical conductivity in ZnCr_2Se_4 can be explained by the existence of higher concentration of the Zn vacancies (playing role of the double acceptor) than the concentration of the Se vacancies.¹¹ The neutron-diffraction studies carried out on the samples of the spinel series $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$ confirm the existence of a few percent of vacancy concentration.¹² The discussion of the electronic structure of the spinel CuCr_2Se_4 (Refs. 7, 13, and 14) seems to be important. Lotgering's idea of the monovalent copper and the mixed valency of the Cr ions (Cr^{3+} , Cr^{4+}) (Ref. 7) turned out to be predominant. This idea was later confirmed by x-ray photoemission spectroscopy (XPS) (Ref. 15), NMR, and neutron diffraction^{16,17} as well as by the studies with the aid of the polarized neutrons carried out on the single-crystal CuCr_2Se_4 .¹⁸

The aim of this paper is the discussion of the experimental data concerning the electrical conductivity and the Seebeck effect in the spinel series $\text{Zn}_{1-x}\text{A}_x\text{Cr}_2\text{Se}_4$ ($A=\text{Cu}, \text{Ga}_{2/3}$) as well as an attempt of the theoretical estimation of both the carrier concentration and mobility and also the Fermi energy in the temperature range of 70–500 K.

II. EXPERIMENT

The polycrystalline samples of the spinel series $\text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ ($x=0.0, 0.01, 0.02, 0.025, 0.05, 0.07, 0.1, 0.2, 0.3, 0.5, 0.7, 0.8, 0.9, 1.0$) and $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$ ($x=0.1, 0.2, 0.3, 0.4, 0.5$) as well as the single-crystal samples of $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$ ($x=0.0, 0.05, 0.04$) served as a material for this paper. The samples of $\text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ ($x=0.01, 0.02, 0.05, 0.07, 0.3$) were kindly delivered by Kusz and the remaining samples by Okonska-Kozłowska. All the details concerning the technology of the samples are described in other papers.^{1,2}

The electrical conductivity measurements of the samples under study were carried out with the aid of the two-point dc method in the temperature range of 70–500 K. The high-Ohmic samples were measured with the use of the electronic resistance bridge.¹⁹ The low-Ohmic samples were measured by applying a direct current to the sample and measuring the voltage drop on it. The polycrystalline samples of the shape of a parallelepiped ($\sim 0.5 \times 3 \times 6$ mm³) were pressed under the pressure of 10–11 MPa, which gave densities of 94 ± 5 % of the x-ray density. The single-crystal samples also had the shape of a parallelepiped ($\sim 0.5 \times 2 \times 3$ mm³) cut out from the octahedral basis making the crystal lattice plane (001). The measurements of the electrical conductivity were performed in the [110] direction with the accuracy of ± 0.6 %. The electrical contacts were made of a silver paste.

The Seebeck effect measurements of the samples under study were carried out with the use of an electronic measuring system generating a temperature difference $\Delta T = T_2 - T_1$ and keeping a constant average temperature $T = (T_1 + T_2)/2$ between the two platinum blocks, where a sample was placed. In these blocks two thermocouples Chromel-Alumel were fixed in order to measure the temperatures T_1 and T_2 . In the range of the temperature difference $0.0 \text{ K} \leq \Delta T \leq 7 \text{ K}$ the dependence of the thermoelectric force on ΔT was linear. From the slope of this straight line the Seebeck-coefficient was determined with the accuracy of $\pm 5 \mu\text{V/K}$. The measurements of ZnCr_2Se_4 were made in the temperature range $120 < T < 320$ K, whereas for the remaining samples they were made at $T = 313 \text{ K}$.^{20,21}

The Hall-effect studies were also performed but the results were not repeatable because the sample thickness was too large and the current-carrier mobility in the spinels was too small. From the measurements of the electrical conductivity versus temperature the following quantities were also determined: (1) the activation energy ($E = E_1, E_2$) for the clearly two straight line intervals of the conductivity curves for the spinels under study from the formula $\sigma = \sigma_0 \exp(-E/kT)$ with the accuracy of

TABLE I. Values of E_1 , E_2 , N_s , and N_d for the spinel series $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$.

x	E_1 (eV)	E_2 (eV)	N_d (m ⁻³)	N_s (m ⁻³)
	Monocrystals			
0.00	0.056	0.482	5.3×10^{21}	8.4×10^{21}
0.05	0.068	0.477	8.2×10^{19}	6.0×10^{20}
0.40	0.183	0.478	3.2×10^{19}	9.8×10^{19}
	Polycrystals			
0.00	0.056	0.200	1.2×10^{21}	2.4×10^{21}
0.10	0.083	0.207	4.6×10^{19}	1.4×10^{20}
0.20	0.092	0.211	3.0×10^{19}	6.9×10^{19}
0.30	0.085	0.211	3.9×10^{19}	1.1×10^{20}
0.40	0.096	0.207	1.9×10^{19}	4.2×10^{19}
0.50	0.098	0.210	9.4×10^{18}	1.9×10^{19}

TABLE II. Values of E_1 , E_2 , N_s , and N_d for the spinel series $Zn_{1-x}Cu_xCr_2Se_4$.

x	E_1 (eV)	E_2 (eV)	N_d (m^{-3})	N_s (m^{-3})
0.00	0.056	0.200	1.2×10^{21}	2.4×10^{21}
0.01	0.034	0.100	1.8×10^{23}	1.1×10^{24}
0.02	0.027	0.086	2.6×10^{23}	1.9×10^{24}
0.025	0.016	0.066	3.2×10^{23}	2.0×10^{24}
0.05	0.0071	0.045	4.6×10^{23}	2.6×10^{24}
0.07	0.0093	0.044	7.0×10^{23}	3.4×10^{24}
0.10	0.0084	0.057	8.2×10^{23}	5.4×10^{24}
0.20	0.0049	0.470	9.9×10^{23}	7.2×10^{24}
0.30	0.0033	-0.0004	4.0×10^{24}	1.2×10^{25}
0.50	-0.0049	-0.0241	1.9×10^{25}	7.8×10^{25}
0.70	-0.0046	-0.0224	4.9×10^{25}	1.7×10^{26}
0.80	-0.0044	-0.0305	5.2×10^{25}	2.4×10^{26}
0.90	-0.0027	-0.0211	1.6×10^{26}	5.0×10^{26}
1.00	-0.0025	-0.0271	2.0×10^{26}	5.8×10^{26}

± 0.0005 eV (see Tables I and II); (2) the values of the thermal coefficient of resistance (TCR) a_{TCR} from the relation $\rho = \rho_0(1 + a_{TCR})$ with the accuracy of $\pm 0.6\%$ of the measured values.

III. RESULTS

The results of electrical conductivity ($\ln\sigma$) measurements as a function of the reciprocal temperature ($10^3/T$) in the spinel series $Zn_{1-x}A_xCr_2Se_4$ ($A = Cu$ or $Ga_{2/3}$) are presented for the polycrystalline samples in Fig. 2 and for the single-crystal samples in Fig. 3. The results of the

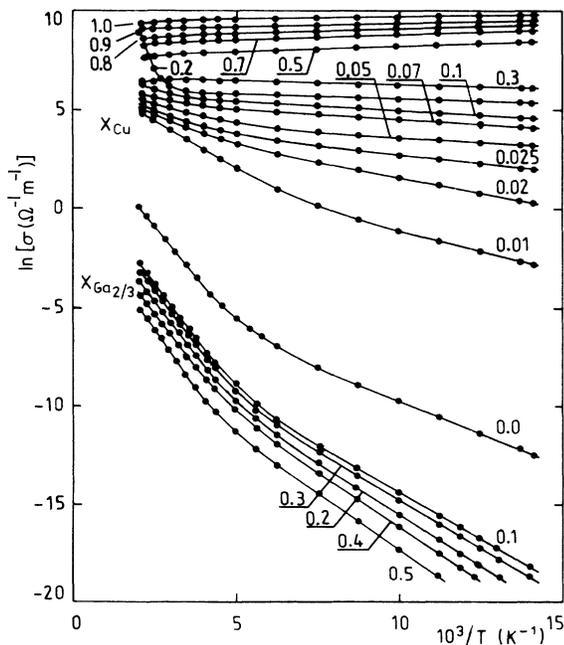


FIG. 2. The electrical conductivity ($\ln\sigma$) vs T^{-1} for the polycrystalline samples of $Zn_{1-x}A_xCr_2Se_4$.

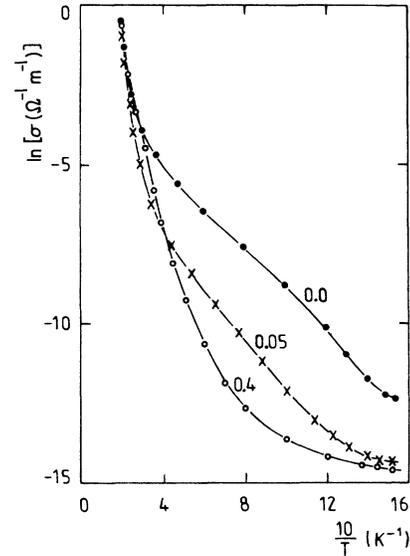


FIG. 3. The electrical conductivity ($\ln\sigma$) vs T^{-1} for the single-crystal samples of $Zn_{1-x}Ga_{2x/3}Cr_2Se_4$.

Seebeck coefficient measurements as a function of concentration x at the temperature of 313 K are presented in Fig. 4. They suggest that all the spinels under study are characterized by the p -type electrical conductivity independently of the type of the substituted cation. In the spinel series $Zn_{1-x}Cu_xCr_2Se_4$ a sudden increase (of about 5 orders of magnitude) of the electrical conductivity and the strong decrease of the Seebeck coefficient with the increase of the Cu ion concentration in the sample at room temperature are observed. A change in the sign of the TCR near $x = 0.3$ is observed, which is linked with the change of the electrical conductivity character from the semiconductive into the metallic one (see Fig. 5). The

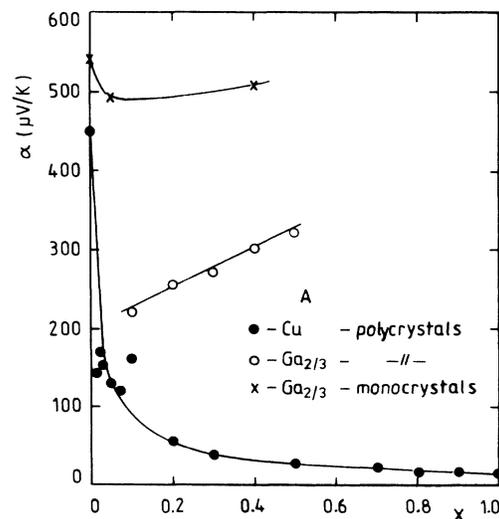


FIG. 4. The Seebeck coefficient α vs x at 313 K in $Zn_{1-x}A_xCr_2Se_4$.

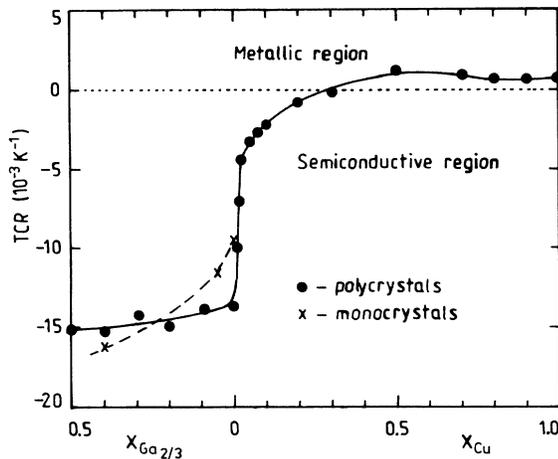


FIG. 5. The temperature coefficient of resistance TCR vs x in $\text{Zn}_{1-x}\text{Ga}_x\text{Cr}_2\text{Se}_4$.

strong increase of the electrical conductivity leading to the semiconductor-metal phase transition suggests that the monovalent copper in the diamagnetic configuration Cu^{1+} ($3d^{10}$) substituted in place of the divalent zinc causes (because of the electrical neutrality condition) the valency change of the Cr ions, i.e., from Cr^{3+} ($3d^3$) to Cr^{4+} ($3d^2$). This change leads to the decrease of the filling degree of the chromium band, which in turn causes the increase of the current carrier transport through the double exchange magnetic interaction linked with the jump of an electron between two ions with the different valence. It gives—as a result—a strong increase of the hole concentration in the mixed valence band of the chromium ions ($\text{Cr}^{3+}, \text{Cr}^{4+}$).

In the spinel series $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$ a decrease of the electrical conductivity and TCR as well as an increase of the Seebeck coefficient with the increase of the Ga ion concentration are observed (see Figs. 2–5). It points to the hole concentration decrease. This effect can be caused by the recombination of the current carriers in the deep vacancy levels lying in the forbidden band. The fact that the substitution of the trivalent gallium in place of the divalent zinc does not lead to the increase of the electrical conductivity and to the change of its type (i.e., from p into n), as is the case in the ferromagnetic spinel CdCr_2Se_4 doped with the trivalent indium,²² can be considered as another argument in favor of the fact that in the spinels with the antiferromagnetic ordering the mixed valence band of the Cr ions is not to be observed.

From the temperature measurements of the Seebeck coefficient α carried out in the spinel ZnCr_2Se_4 (see Fig. 6) it follows that α strongly increases with the temperature increase. Simultaneously, this effect, along with the strong increase of the electrical conductivity with temperature (see Fig. 2), points to the stronger temperature dependence of the hole mobility than of their concentration. In the opposite case, as it is predicted by the theory of semiconductors for the carriers of one type, α should decrease with the increase of the hole concentration.²³

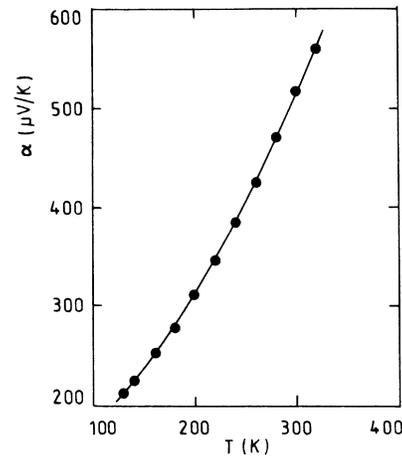


FIG. 6. The Seebeck coefficient α vs T in ZnCr_2Se_4 .

Moreover, the shape of the electrical conductivity curves, in particular, in the case of the single crystals of $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$, is characteristic of the dielectrics, which have two or more values of the activation energy and where the mobility of the current carriers is a strongly thermally activated process.

IV. THE PROCEDURE OF CALCULATIONS

Because of the difficulties in obtaining reliable experimental results concerning the Hall effect in the spinels under study, and because of the lack of more extensive data, an attempt was made to theoretically evaluate the Fermi energy E_F , the mobility μ , and the concentration p of the current carriers, on the basis of the experimental data concerning the electrical conductivity and the Seebeck effect in these spinels. A procedure described in Ref. 24 was used for it, in which the following assumptions were made: (a) the extrinsic electrical conductivity is of one type (p type); (b) the zinc vacancies (playing role of the double acceptor¹¹) make the acceptor levels; (c) there are two independent acceptor levels with the different activation energies (E_{a_1} and E_{a_2}).

We take into account, as well as writing about, the well-known formulas of the hole concentration p in the valence band and of the concentration N_i of the doubly occupied acceptor levels, as explained in the following:

$$p = N_v \exp[-(\bar{\mu} - E_v)/kT], \quad (1)$$

$$N_i = \frac{N_s}{1 + 2 \exp[(E_{a_1} - \bar{\mu})/kT]} + \frac{N_d}{1 + 2 \exp[(E_{a_2} - \bar{\mu})/kT]}, \quad (2)$$

where $N_v = (2\pi mkT/h^2)^{3/2}$, m is the effective mass, h is Planck's constant, $\bar{\mu}$ is the chemical potential, k is Boltzmann's constant, E_v is the energy of the top of the valence band, N_s is the concentration of the acceptor shallow levels, N_d is the concentration of the acceptor deep levels, and E_{a_1}, E_{a_2} are the energies of the shallow

and deep acceptor levels, respectively, counted from the top of the valence band.

Substituting

$$E_{a_2} - E_v = E_1, \quad (3)$$

$$E_{a_1} - E_v = E_2, \quad (4)$$

$$\bar{\mu} - E_v \equiv E_F, \quad (5)$$

where E_F is a certain averaged values of the Fermi energy and giving the condition of the electrical neutrality $p = N_i$, the following equation of the third order was obtained:²⁵

$$Ay^3 + By^2 + Cy + D = 0, \quad (6)$$

where

$$y = \exp(-E_F/kT),$$

$$A = 4N_v \exp[(E_1 + E_2)/kT],$$

$$B = 2N_v [\exp(E_1/kT) + \exp(E_2/kT)],$$

$$C = N_v - [N_d 2 \exp(E_1/kT) + N_s 2 \exp(E_2/kT)],$$

$$D = -(N_s + N_d).$$

To solve Eq. (6) the values of the parameters m, N_s, N_d are necessary.

The effective mass m of the hole was evaluated from the following formula:²⁶

$$\frac{m}{m_0} \cong \frac{3}{20}(E_g + \Delta), \quad (7)$$

where m_0 is the rest mass of the electron, E_g is the width of the energy gap, and Δ is the spin-orbit splitting.

The value of the spin-orbit splitting in the spinels under study is approximately equal to zero, because the crystal field "freezes" the orbital magnetic moment.⁶ The value of the energy gap experimentally determined at room temperature in the spinel ZnCr_2Se_4 is equal to $E_g = 1.285$ eV (Ref. 27) and is practically independent of the temperature above 70 K. Therefore, the value of the effective mass of the hole calculated from (7) was assumed. This value is equal to $m = 0.19275m_0$. The values N_s and N_d were estimated from the condition

$$\frac{\sigma(T)}{\sigma(300 \text{ K})} = \frac{p(T)}{p(300 \text{ K})} \quad (8)$$

for the corresponding straight line segments of the $\ln \sigma$ versus $10^3/T$ curve. p was determined from the formula²⁸

$$p = N_v \left[-1 + \left[1 + \frac{8 \exp(E/kT)N}{N_v} \right]^{1/2} \right] \times [4 \exp(E/kT)]^{-1}, \quad (9)$$

where $N = N_s$ and $E = E_1$ for the shallow acceptor levels, $N = N_d$ and $E = E_2$ for the deep acceptor levels.

The values $N_s, N_d, E_1,$ and E_2 are presented in Tables I and II. Knowing the values $m, N_s,$ and N_d as well as

E_1 and E_2 it was possible to solve Eq. (6) by the Warmus method²⁹ with the use of a Schneider CPC 6128 micro-computer. From the three roots of Eq. (6), the one having the physical meaning was positive and the two others were negative. The following formulas for the current carrier concentration p , their mobility μ , and the Fermi energy E_F were obtained:

$$p = N_v y_1, \quad (10)$$

$$\mu = \frac{\sigma}{e N_v y_1}, \quad (11)$$

$$E_F = k \ln(1/y_1), \quad (12)$$

where e is the elementary charge and y_1 is the only positive solution of the Eq. (6) determined with the accuracy $< 1.9 \times 10^{-10}|R|$. The value of R was evaluated from the formula²⁹

$$R = \{ [1/(9A^2)][2B^2(B^2 - C) - 3A(BC - D)] \}^{1/3}.$$

R is at most of the order 10^7 . Therefore, the maximal error of y_1 is less than 1.9×10^{-3} .

V. RESULTS OF CALCULATIONS

The calculated values of $p, \mu,$ and E_F as a function of the concentration x at 300 K for the polycrystalline samples of the series $\text{Zn}_{1-x}\text{A}_x\text{Cr}_2\text{Se}_4$ are presented in Fig. 7. The temperature dependence of p and μ for the single-crystal samples is presented on Fig. 8 and for the polycrystalline samples in Figs. 9 and 10. Figure 11 presents the difference between the Fermi level and the intrinsic value E_i as a function of temperature T and concentration x .

In the spinel series $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$ the increase of the Ga concentration in the sample leads to the decrease of both the hole concentration and their mobility as well as to the increase of the Fermi energy. The calculated value of the hole mobility at 300 K is very small and equal to $\sim 1 \times 10^{-4} \text{ m}^2/\text{Vs}$. This value is comparable

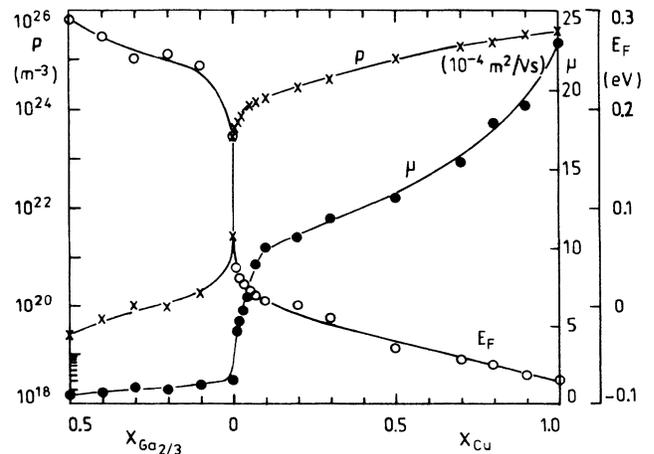


FIG. 7. The dependence of $p, \mu,$ and E_F on x at 300 K in $\text{Zn}_{1-x}\text{A}_x\text{Cr}_2\text{Se}_4$.

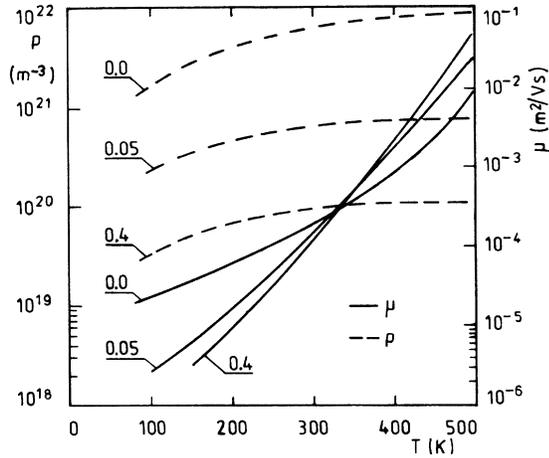


FIG. 8. The temperature dependence of p and μ for the single-crystal samples of $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$.

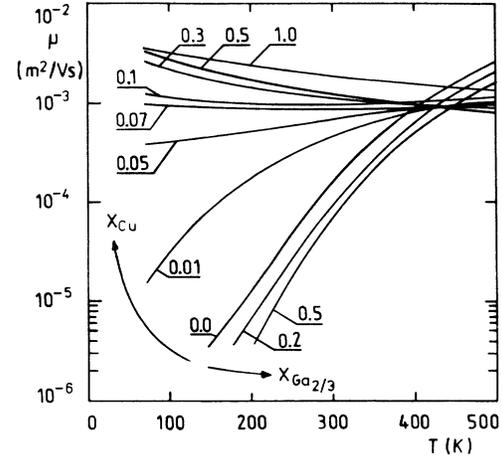


FIG. 10. The temperature dependence of μ for the polycrystalline samples of $\text{Zn}_{1-x}\text{A}_x\text{Cr}_2\text{Se}_4$.

with the experimental values obtained from the Hall-effect study in the spinel ZnCr_2Se_4 .^{9,11} As it follows from the p versus T and μ versus T curves, one observes a stronger temperature dependence of the current carrier mobility than of their concentration, which suggests that the temperature dependence of μ is the thermally activated process which is stronger than the one concerning p . The decrease of the difference ($E_F - E_i$) with the increase of both the temperature and the Ga concentration

in the sample points to the increased contribution of the intrinsic conductivity in the spinels $\text{Zn}_{1-x}\text{Ga}_{2x/3}\text{Cr}_2\text{Se}_4$. The values $E_F - E_i$ for the corresponding single-crystal samples are somewhat greater, which is connected with the relatively higher hole concentration. The increase of both the intrinsic conductivity and the Seebeck coefficient corresponds with the increase of x and points to the lowering of the hole concentration. It is because of the charge compensation linked with the recombination of the current carriers, which takes place throughout the localized states situated in the forbidden band. The nature of these states can be linked with the existence of the structure defects, whose energy levels lie in the forbidden band. Such levels, which are situated closer to the middle of the forbidden band (i.e., E_i) than to the top of the valence band, make, in general, so-called recombination

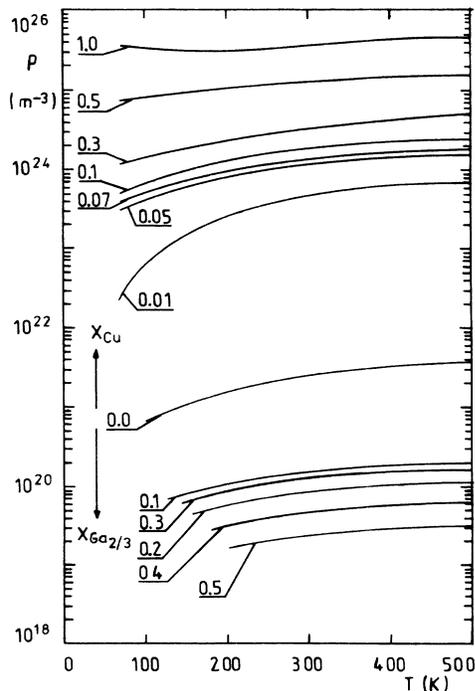


FIG. 9. The temperature dependence of p for the polycrystalline samples of $\text{Zn}_{1-x}\text{A}_x\text{Cr}_2\text{Se}_4$.

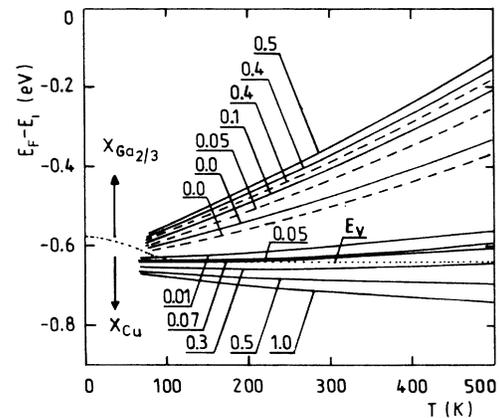


FIG. 11. The difference between the Fermi level E_F and the intrinsic value E_i as a function of temperature T and concentration x for the polycrystalline (solid line) and the single-crystal (dashed line) samples of $\text{Zn}_{1-x}\text{A}_x\text{Cr}_2\text{Se}_4$. The dotted line represents the dependence $E_v = f(T)$ estimated from Ref. 27.

centers, which contribute very weakly to the generation of the current carriers.

In the spinel series $Zn_{1-x}Cu_xCr_2Se_4$ one observes a strong increase of the hole concentration, a slight increase of their mobility, and a lowering of the Fermi energy with the increase of Cu concentration in the sample. The temperature dependence of the hole concentration is weaker and weaker with the increase of Cu concentration in the sample, whereas the temperature dependence of the hole mobility is more complex. Thus for small x one observes a strong increase of the hole mobility with the increase of temperature. For the spinels with the copper concentration of $x = 0.07$ and 0.1 the hole mobility is approximately temperature independent. On the other hand, for the spinels with the high copper concentration in the sample one observes a decrease of the hole mobility with the increase of temperature.

The increase of the difference $E_F - E_i$ with the increase of both temperature and copper concentration points to a greater contribution of the extrinsic conductivity in this spinel series. The increase of the extrinsic conductivity and the decrease of the Seebeck coefficient with the increase of x points to the increase of the hole concentration connected with the double exchange magnetic interaction. The increase of the hole concentration in the mixed valence band of chromium ions is so strong, that it leads, starting from copper concentration of $x = 0.05$, to the partial degeneracy of the semiconductive state of the spinels $Zn_{1-x}Cu_xCr_2Se_4$.

VI. DISCUSSION

The substitution in place of divalent Zn in the spinel $ZnCr_2Se_4$ of either monovalent Cu or trivalent Ga leads to the diametrically different electrical properties. For the high Cu concentrations one observes high electrical conductivity, typical of metals, whereas for the high Ga concentrations one observes low electrical conductivity, typical of dielectrics. The range of values of the electrical conductivity at room temperature between the boundary spinels of the series $Zn_{1-x}A_xCr_2Se_4$ (i.e., for $x = 0.5$ $Ga_{2/3}$ and for $x = 1.0$ Cu) is equal to about 7 orders of magnitude. Such a big change of the electrical conducti-

ty in the spinel series under study can be qualitatively explained based on the band-structure sketches presented in Fig. 12. As it follows from the calculations, the Fermi level rises with the increase of the Ga^{3+} -ion concentration and drops with the increase of the Cu^{1+} -ion concentration in the sample of the series $Zn_{1-x}A_xCr_2Se_4$. In the first case [Figs. 12(a) and 12(b)] the vacancy levels become deeper leading to the recombination of the current carriers and to the decrease of the electrical conductivity. Moreover, the chromium ion band ($2Cr^{3+}$) is fully occupied. In the second case [Fig. 12(c)] the drop of the Fermi level E_F leads to the decrease of the occupation of the $2Cr^{3+}$ ion band which—in the situation of the diamagnetic configuration of the Cu ions ($3d^{10}$) (Ref. 15) and of the electrical neutrality condition—is connected with the appearance of the mixed valence of the chromium ions (Cr^{3+}, Cr^{4+}). The mixed valence band of the chromium ions (Cr^{3+}, Cr^{4+}) is the main source of the increase of the hole concentration. The mechanism of the double exchange magnetic interaction, resulting in the jump of an electron between Cu^{3+} and Cr^{4+} ions, strongly contributes to the observed increase of the electrical conductivity and to the change of its character from the semiconductive into the metallic one. Figure 12(c) for the boundary spinel $CuCr_2Se_4$ corresponds to the Lotgering model,⁷ in which the mixed valence band of the chromium ions is half-fully occupied and the ion concentration ratio $[Cr^{3+}]/[Cr^{4+}]$ is equal to 1.

Both the experimental results and calculations suggest that, in the spinels under study, the changes of the electrical conductivity are caused by the changes of both the concentration and the mobility of the current carriers. It testifies that the two mechanisms are the processes thermally activated.

The magnetic properties of the spinels under study are characterized by the variety of the magnetic structures, but all these spinels have one feature in common: only positive signs of the paramagnetic Curie-Weiss temperature Θ_{CW} , which makes a measure of the strength of the short-range magnetic interactions leading to the fer-

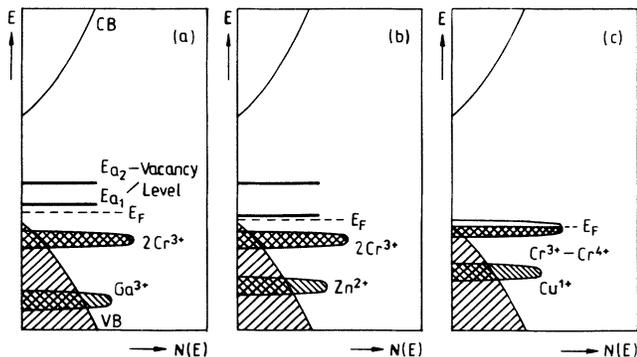


FIG. 12. The band-structure sketches for (a) $Zn_{1-x}Ga_{2x/3}Cr_2Se_4$, (b) $ZnCr_2Se_4$, and (c) $Zn_{1-x}Cu_xCr_2Se_4$.

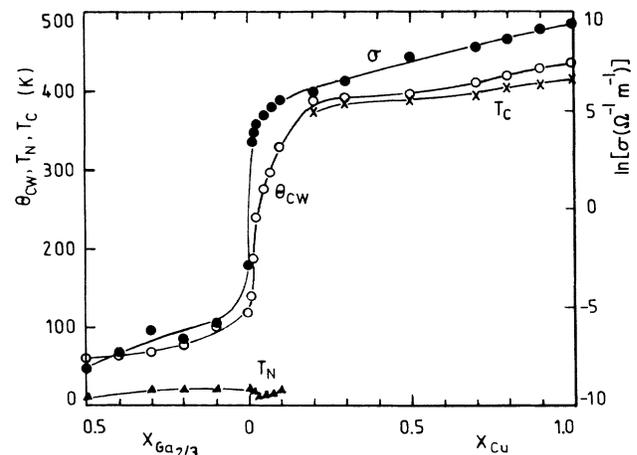


FIG. 13. The dependence of Θ_{CW} , T_N , T_C (Refs. 3 and 4), and $\ln\sigma_{(300\text{ K})}$ on x in $Zn_{1-x}A_xCr_2Se_4$.

romagnetic ordering of the magnetic moments of the Cr ions. It turns out that Θ_{CW} increases with the decrease of the Ga concentration (down to $x=0$) and increases further with the increase (from $x=0$) of the Cu concentration in the sample of the spinel series $Zn_{1-x}A_xCr_2Se_4$ ($A=Cu, Ga_{2/3}$).^{3,4} This dependence, as well as the dependence of the electrical conductivity ($\ln\sigma_{300K}$) on concentration x , are presented in Fig. 13. They are strikingly similar and make a beautiful example of the correlation of the magnetic and electrical properties. Just for comparison in Fig. 13 the Néel (T_N) and the Curie (T_C) temperatures are also marked. One can see in Fig. 13 that the higher the value of the paramagnetic Curie-Weiss temperature, the higher the value of the electrical conductivity. It suggests that in the case of the domination of the antiferromagnetic component of the ordering of the magnetic moments (i.e., for small values of Θ_{CW}) one observes the low electrical conductivity (typical of dielectrics) and the state corresponding to the compensated semiconductors. On the other hand, in the case of the ferromagnetic ordering of the magnetic moments (i.e., for

high values of Θ_{CW}) one observes the high electrical conductivity (typical of metals) and the state of the partial degeneracy. For the intermediate values of Θ_{CW} one observes both the electrical conductivity typical of semiconductors and the complex magnetic structures (e.g., simple spiral, ferromagnetic spiral, spin glass, etc.) being, in principle, a result of the competition of the antiferromagnetic and ferromagnetic interactions (in this case superexchange and double exchange).

Summing up, one has to conclude that the valence of the substituted cations occupying the tetrahedral sites in the structure of the spinels under study strongly affects their electrical properties.

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