The Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$—Single Crystals Obtained by Chemical Vapour Transport—Structure and Magnetic, Electrical, and Thermal Properties

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Abstract: Monocrystalline chalcogenide spinels ZnCr$_2$Se$_4$ are antiferromagnetic and semiconductor materials. They can be used to dope or alloy with related semiconducting spinels. Therefore, their Pb-doped display is expected to have unique properties and new potential applications. This paper presents the results of dc and ac magnetic measurements, including the critical fields visible on the magnetisation isotherms, electrical conductivity, and specific heat of the ZnCr$_2$S$_4$Pb single crystals. These studies showed that substituting the diamagnetic Pb ion with a large ion radius for the Zn one leads to strong short-range ferromagnetic interactions in the entire temperature range and spin fluctuations in the paramagnetic region at $H_{dc} = 50$ kOe.

Keywords: chalcogenides; X-ray study; magnetic and electrical properties; specific heat; thermal analysis

1. Introduction

Magnetic and semiconductor spinels are of great interest because of their exotic phenomena and the fascinating ground states observed at the turn of the 20th and 21st centuries, such as [1]: behaviour of heavy fermions [2,3], complex spin order and spin dimerization [4–6], spin-orbital fluid [7,8], orbital glass [9], the coexistence of ferromagnetism and ferroelectricity [10–12], the so-called Jahn–Teller effect [13–15], and phenomena attributed to the competing exchange of ferromagnetism (FM) and anti-ferromagnetism (AFM) of almost equal strength, causing a strong bond frustration [16].

Many interesting properties were observed in the spinel series that fulfil Vegard’s law in the full-concentration region. In the Katowice group at the end of the 20th century, the Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$ spinel series was particularly intensively studied, the edge spinels of which ZnCr$_2$Se$_4$ and CuCr$_2$Se$_4$ were respectively antiferromagnet and ferromagnet, and at the same time, a semiconductor and a conductor [17–19]. In the early 2000s, Parker et al. [20] discovered a transition from positive to negative magnetoresistance there.

Single crystals are used in modern, innovative technology and the electronic industry. The semiconducting [21] and antiferromagnetic [22] ZnCr$_2$Se$_4$ spinel is a matrix for various diluted systems where the effects of the site disorder, lattice frustration, and random distribution of spin interactions [23] create novel potential applications in spin-based electronic technology. In ZnCr$_2$Se$_4$, the spin order occurring at the Neél temperature
\( T_N = 21 \text{ K} \) [1] is an incommensurate spiral due to the narrow distances between Cr ions. Still, the larger ones cause ferromagnetic (FM) interactions confirmed by the positive Curie–Weiss temperature of \( \theta = 90 \text{ K} \) [21,22]. For this reason, differences in magnetic interactions between the nearest and farther neighbours in \( \text{ZnCr}_2\text{Se}_4 \) are related to the frustration of chemical bonds that play an essential role. The magnetic order is accompanied by structural transformation from cubic \( Fd\overline{3}m \) to tetragonal \( I\overline{4}/amd \) symmetry with a slight contraction along the \( c \) axis [24,25], manifested by sharp first-order anomalies at \( T_N \) on the specific heat curve [1].

Our group’s work has been done based on the \( \text{ZnCr}_2\text{Se}_4 \) matrix. This matrix has been doped with both non-magnetic ions, such as, for example, \( Al \) [26–28], \( Cu \) [17–19,29,30], \( \text{Ga} \) [17,18,31–33], \( \text{Sn} \) [35,36], and \( \text{Ta} \) [37], and with magnetic ones, such as, for example, \( \text{Dy} \) [38,39], \( \text{Gd} \) [40], \( \text{Ho} \) [41], \( \text{Mn} \) [42,43], \( \text{Nd} \) [44], and \( \text{Ni} \) [45]. All the above-mentioned doped spinels have two features in common. They are semiconductors and antiferromagnets, just like a matrix. An interesting feature is the appearance of the re-entrant-type spin-glass when non-magnetic \( \text{Al} \) [27] and \( \text{Sn} \) [36] ions are located in the octahedral sites of the spinel structure. It was also observed that \( \text{Sn} \) ions occupying octahedral sites reduce the \( n \)-type electrical conductivity by magnitude compared to samples in which they occupy tetrahedral ones [35]. This interesting phenomenon has been explained based on the quantum band model, which predicts a lowering of the Fermi level in the lowest \( \text{Cr}^{3+} \)–Mott–Hubbard sub-band with a narrowed \( 3d^3 \, t_{2g} \) band, which gives an increase in the energy gap when \( \text{Sn}^{3+} \) ions (spin defects) are replaced at octahedral sites instead of \( \text{Cr}^{3+} \) ones [35]. Interestingly, geometric spin-glass was observed when substituting \( \text{Dy} \) ions, a paramagnetic rare-earth ion in both tetrahedral and octahedral positions [39].

This work continues our research that involved introducing the p-block element into the crystal lattice \( \text{ZnCr}_2\text{Se}_4 \). Pb belongs to group 14 of the periodic table. \( \text{Sn} \) also belongs to this group. \( \text{ZnCr}_2\text{Se}_4 \) single crystals doped with tin showed the phenomenon of spin-glass [36]. It was assumed that the presence of \( \text{Pb} \) ions in the \( \text{ZnCr}_2\text{Se}_4 \) crystal lattice would affect the physicochemical properties of the parent compound. A single crystal growth model was developed using a computer programme. The structural, magnetic, electrical, and thermal properties were determined using various methods (XRD—X-ray Diffraction, SEM—Scanning Electron Microscopy, DSC—Differential Scanning Calorimetry, TG—Thermogravimetry, SQUID—Superconducting Quantum Interference Device, QD-PPMS—Quantum Design Physical Property Measurement System). This work presents the structural, magnetic, electrical, thermal, and specific heat properties of five monocrystalline samples doped with diamagnetic \( \text{Pb}^{2+} \) ions with a large ion radius instead of \( \text{Zn}^{2+} \) ones. The novelty of this work is the study of the ac magnetic susceptibility measured in an external dc magnetic field up to 50 kOe. According to our knowledge, such crystals have not been described in the literature.

2. Materials and Methods

High-purity elements, \( \text{Zn} \), \( \text{Pb} \), \( \text{Cr} \), \( \text{Se} \) (5N, Sigma Aldrich, Sofia, Bulgaria), and anhydrous \( \text{CrCl}_3 \) (Sigma Aldrich), were applied to synthesise \( \text{ZnCr}_2\text{Se}_4 \) single crystals doped with \( \text{Pb} \).

2.1. Computation of Thermodynamic Parameters for the Chemical Transport Reactions

The basis for the growth of single crystals by gaseous chemical transport is reversible transport reactions. The criterion determining the reaction’s transport capacity is the order of magnitude of the equilibrium constant \( K_p \). The \( K_p \) value should be close to 1 (\( \log K_p \approx 0 \)). The following dependence is used to assess the transport capacity of the reaction:

\[
\Delta G^0_T = \Delta H^0_{298K} - T \Delta S^0_{298K}
\]

where \( \Delta H^0_{298K} \) and \( \Delta S^0_{298K} \) are the corresponding changes of the reaction’s standard and enthalpy and entropy. Free energy variations can be used to assess the transportability of
the reaction $\Delta G^0$ instead of the equilibrium constant $K_p$ because these quantities are related to the formula:

$$\Delta G^0 = -2.303RT \log K_p = \Delta H^0 - T\Delta S^0,$$

(2)

where: $R$—gas constant; $T$—absolute temperature; $K_p$—equilibrium constant; $\Delta H^0$, $\Delta S^0$—changes in the reaction’s free energy, enthalpy, and entropy. Accompanying reactions related to the solvent or reaction products’ dissociation may occur during the transport process. Therefore, all independent reactions occurring in the tested system should be considered. The selection of an appropriate transport substance involves finding such transport reactions for which the values of $K_p$ or $\Delta G^0$, in the selected temperature range, do not deviate too much from the equilibrium values. We are looking for a substance that will produce sizeable partial pressure differences $\Delta p$, with the slightest possible temperature difference.

In the process of selenium chromite single crystal growth, anhydrous CrCl$_3$ is used, which dissociates at a temperature above 773 K according to the following reactions [46,47]:

$$2\text{CrCl}_3(\text{g}) = 2\text{CrCl}_2(\text{g}) + \text{Cl}_2(\text{g}),$$

$$\text{CrCl}_2(\text{g}) + \text{Cl}_2(\text{g}) = \text{CrCl}_4(\text{g}).$$

In a closed system, in a gas solution, apart from CrCl$_3$ and Cl$_2$, there is also CrCl$_4$. Therefore, the dissociation products should be taken into account when creating a set of all independent transport reactions that occur simultaneously in the ZnSe–PbSe–CrCl$_3$ system:

$$2\text{ZnSe} + 4\text{CrCl}_3(\text{g}) = 2\text{ZnCl}_2(\text{g}) + 4\text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{ZnSe} + 4\text{CrCl}_3(\text{g}) = \text{Zn}_2\text{Cl}_4(\text{g}) + 4\text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{PbSe} + 2\text{CrCl}_3(\text{g}) = 2\text{PbCl}_2(\text{g}) + 2\text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{PbSe} + 4\text{CrCl}_3(\text{g}) = 2\text{PbCl}_2(\text{g}) + 4\text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{ZnSe} + 2\text{CrCl}_4(\text{g}) = 2\text{ZnCl}_2(\text{g}) + 2\text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{ZnSe} + 2\text{CrCl}_4(\text{g}) = \text{Zn}_2\text{Cl}_4(\text{g}) + 2\text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{PbSe} + \text{CrCl}_4(\text{g}) = 2\text{PbCl}_2(\text{g}) + \text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{PbSe} + 2\text{CrCl}_4(\text{g}) = 2\text{PbCl}_2(\text{g}) + 2\text{CrCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{ZnSe} + 2\text{Cl}_2(\text{g}) = 2\text{ZnCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{ZnSe} + 2\text{Cl}_2(\text{g}) = \text{Zn}_2\text{Cl}_4(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{PbSe} + \text{Cl}_2(\text{g}) = 2\text{PbCl}_2(\text{g}) + \text{Se}_2(\text{g})$$
$$2\text{PbSe} + 2\text{Cl}_2(\text{g}) = 2\text{PbCl}_2(\text{g}) + \text{Se}_2(\text{g})$$

These hypothetical reactions were used to calculate the temperature dependence of the thermodynamic parameters ($\Delta H^0$, $\Delta G^0$, $\Delta S^0$, and $\log K_p$). The calculations were performed using the H.S.C. Chemistry 6 computer programme. Based on these calculations, the reaction conditions (dissolution zone temperatures and crystallisation and their difference (Table 1)) make it possible to obtain good-quality crystals.

**Table 1.** Conditions of growth and chemical composition of ZnCr$_2$Se$_4$-Pb single crystals.

| N° | Amounts of Substrates (mmol) | $T_d$ (K) | $T_c$ (K) | $\Delta T$ (K) | $\%$ Weight | Chemical Formula |
|----|-----------------------------|----------|----------|---------------|-------------|-----------------|
|    | $n_{\text{ZnSe}}$ | $n_{\text{PbSe}}$ | 1223 | 1163 | 60 | 12.31 ± 0.09 | 3.23 ± 0.06 | 20.66 ± 0.01 | 63.71 ± 0.04 | Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ |
| (1) | 14.4 | 1.6 | 1133 | 1083 | 50 | 12.25 ± 0.08 | 2.95 ± 0.07 | 20.45 ± 0.02 | 64.54 ± 0.05 | Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ |
| (2) | 14.4 | 1.6 | 1203 | 1153 | 50 | 12.05 ± 0.06 | 3.43 ± 0.06 | 20.49 ± 0.05 | 64.10 ± 0.03 | Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ |
| (3) | 12.8 | 3.2 | 1203 | 1143 | 60 | 11.63 ± 0.02 | 4.51 ± 0.04 | 20.30 ± 0.06 | 63.56 ± 0.03 | Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ |
| (4) | 12.8 | 3.2 | 1203 | 1153 | 50 | 11.42 ± 0.03 | 4.98 ± 0.05 | 20.15 ± 0.03 | 63.42 ± 0.03 | Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ |
| (5) | 11.2 | 4.8 | 1203 | 1153 | 50 | 11.42 ± 0.03 | 4.98 ± 0.05 | 20.15 ± 0.03 | 63.42 ± 0.03 | Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ |

Chemical compositions were determined using Scanning Electron Microscopy. $T_d$ is the temperature of the dissolution zone, $T_c$ is the temperature of the crystallisation zone, and $\Delta T$ is the difference in temperatures between the dissolution and the crystallisation zones.
2.2. Synthesis of ZnSe and PbSe

The polycrystalline ZnSe and PbSe were obtained by the high-temperature sintering of powders (1073 K) using a solid-state reaction in a high vacuum (10^{-5} mbarr).

2.3. Crystal Structure and Chemical Composition

The X-ray diffraction measurement was carried out at 293(1) K. Five samples with different nominal Pb content were selected under a stereoscopic Zeiss optical microscope. A small crystal (diameter of about 0.1 mm) was mounted on a glass capillary. The data were collected using a SuperNova X-ray diffractometer with a microfocus X-ray tube, optimised multi-layer optics for Mo-Kα (λ = 0.71073 Å) radiation, and an Atlas CCD detector. Accurate cell parameters were determined and refined with CrysAlisPro software (Version 1.171.37.35, Agilent Technologies, Wrocław, Poland, 2014). Moreover, the CrysAlisPro program was used to integrate the collected data. The spinel structure (space group no. 227) was refined using the SHELXL-2013 program [48]. All atoms were refined with anisotropic displacement parameters. The chemical composition of the single crystals was studied using a Scanning Electron Microscope JEM 6480 equipped with an energy-dispersive X-ray spectrometer (SEM/EDS). The solid elements (Zn, Pb, Cr, Se) were used as standards to determine the mass % content of the elements in the sample. Measurements were carried out at 20 locations of the single crystal to determine the average chemical composition. Each of the measuring areas was approximately 50 × 30 µm. Then, the average chemical composition was calculated, which is shown in Table 1. The error bar represents the standard deviation. Relatively low values of the standard deviation indicate good homogeneity of the chemical composition.

2.4. Magnetic and Electrical Measurements

Dynamic ac magnetic susceptibility, $\chi_{ac}$, was measured in the temperature range 2–300 K and at an internal oscillating magnetic field $H_{ac} = 1$ Oe, with an internal frequency $f = 120$ Hz taken at external static dc magnetic fields $H_{dc} = 0, 10, 20, 30, 40, \text{ and } 50$ kOe. Magnetisation isotherms, $M(H)$, were measured at 2, 10, 20, 40, 60, and 300 K and in the static magnetic field up to 70 kOe. A Quantum Design MPMS-XL-7AC SQUID magnetometer (Quantum Design, San Diego, CA, USA) was used. The Néel ($T_N$) and $T_m$ temperatures and the critical fields were defined as the extremes corresponding to the derivative of $d\chi_{ac}/dT$ vs. $T$ and $dM/dH$ vs. $H$. The effective magnetic moment was calculated using the equation [37,42,49]: $\mu_{eff} = 2.828\sqrt{C}$, where $C$ is the Curie constant. The magnetic superexchange integrals for the first two coordination spheres, $J_1$ and $J_2$, were calculated using the Holland and Brown equations [50]: $J_1 = ( -9T_N + \theta )/60$ and $J_2 = (3T_N + \theta )/120$. The electrical conductivity, $\sigma(T)$, was measured by the dc method using a KEITHLEY 6517B Electrometer/High Resistance Meter (Keithley Instruments, L.L.C., Solon, OH, USA) in the temperature range of 77–400 K. The activation energy, $E_a$, was determined below room temperature and in the temperature range of 300–400 K from the formula $\sigma = \sigma_0 \exp(-\frac{E_a}{kT})$, where $k$ is the Boltzmann constant and $\sigma_0$ is the reference conductivity. The details of methods used to determine the electrical properties, thermal analysis, and specific heat are described in [37,39,41,44].

3. Results and Discussion

3.1. Growth of Single Crystals and Chemical Composition

Thermodynamic calculations indicate that, for the ZnSe–PbSe–CrCl₃ system, the simultaneous transport of ZnSe and PbSe will be realised using gaseous CrCl₃ and CrCl₄ ($\log K_p$ and $\Delta G^0$ values are close to zero in the selected temperature range: 1000–1400 K). It is shown in Figures 1 and 2 that, for chemical reactions with CrCl₃ and CrCl₄, the enthalpy values are positive ($\Delta H^0 > 0$), which indicates that the transport takes place from a higher temperature to a lower temperature in the direction of the formation of products.

On the other hand, the enthalpy values for the transport of reactions with chlorine (Cl₂) are negative ($\Delta H^0 < 0$), which indicates that the reaction equilibrium is shifted towards the
reactants. Based on these calculations, it has been confirmed that in the ZnSe–PbSe–CrCl$_3$ system, ZnSe and PbSe are mainly transported by gaseous CrCl$_3$ and CrCl$_4$. Values of log$K_a$ are close to zero in the selected temperature range: 1000–1400 K (Figure 3).

Figure 1. The dependence of the thermodynamic parameters vs. temperature $T$ for the ZnSe and PbSe with CrCl$_3$ as a transport agent.
Figure 2. The dependence of the thermodynamic parameters vs. temperature $T$ for the ZnSe and PbSe with $\text{CrCl}_4$ as a transport agent.

Figure 3. The dependence of the thermodynamic parameters vs. temperature $T$ for the ZnSe and PbSe with $\text{Cl}_2$ as a transport agent.
Synthesis of single crystals of $\text{Zn}_{1-x}\text{Pb}_x\text{Cr}_2\text{Se}_4$ was carried out according to the reaction:

$$4(1 - x)\text{ZnSe} + 4x\text{PbSe} + 2\text{CrCl}_3 = \text{Zn}_{1-x}\text{Pb}_x\text{Cr}_2\text{Se}_4 + 3(1 - x)\text{ZnCl}_2 + 3x\text{PbCl}_2$$

for $x = 0.1, 0.2, 0.3$.

Thermodynamic calculations determined the reaction conditions, such as dissolution and crystallisation temperatures, and their difference. The crystallisation zone temperature was between 1083 and 1153 K. The dissolution zone was between 1133 and 1233 K. Their difference was 50–70 K. Based on our experience with the growth of doped $\text{ZnCr}_2\text{Se}_4$ single crystals, we can state that a minor temperature difference ($\Delta T$) is more favourable for crystal growth. Stoichiometric mixtures of the ZnSe, PbSe, and CrCl$_3$ were introduced to quartz ampoules (length—200 mm, inner diameter—20 mm) evacuated to $10^{-5}$ mbarr. The sealed ampoules were placed in a two-zone tubular furnace and heated for 450 h. After heating, the ampoules were cooled at about 70 degrees per hour. Such a preparation process for the growth of single crystals allowed for obtaining single crystals of good quality (Figure 4). Five single crystals with various Pb content were chosen for X-ray diffraction measurements. The reaction conditions and results of SEM analysis, together with determined chemical formulae, are shown in Table 1.

3.2. Structural Study

Based on the structure of $\text{ZnCr}_2\text{Se}_4$, in which the Zn$^{2+}$ ions occupy the tetrahedral position 8a: 1/8, 1/8, 1/8 (A-site), and the Cr$^{3+}$ ions occupy the position 16d: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (B-site), according to the spinel structure, we considered two models of cation distribution. In the first model, the presence of Pb$^{2+}$ ions in A-sites was assumed with coupled site occupancy factors (SOF) and constrained atomic displacements. The second model assumed that the Pb$^{2+}$ ions would substitute the Cr$^{3+}$ ones. Because of the strong correlation, the SOFs for Cr and Pb were refined separately in alternative calculations. The assumed oxidation state of Pb and the correlations of the refined parameters caused the rejection of the second model.

![Figure 4](image-url)

**Figure 4.** (a) A part of quartz ampoule with obtained $\text{ZnCr}_2\text{Se}_4$:$\text{Pb}$ single crystals. Examples of single crystals obtained in the $\text{ZnCr}_2\text{Se}_4$:$\text{Pb}$ system: (b) $\text{Zn}_{0.94}\text{Pb}_{0.06}\text{Cr}_2\text{Se}_4$, (c) $\text{Zn}_{0.92}\text{Pb}_{0.08}\text{Cr}_2\text{Se}_4$, (d) $\text{Zn}_{0.88}\text{Pb}_{0.12}\text{Cr}_2\text{Se}_4$.

Based on this refinement, the first model allowed us to obtain the acceptable atomic displacement parameters and SOFs. We could describe the general chemical formula for
obtained single crystals as presented in Tables 2 and 3. The observed slight increase in thermal shift at the A-site points out a static disturbance in the location of the Zn$^{2+}$/Pb$^{2+}$ pseudo-ion, which is usually caused by the difference in ionic charges and in ionic and covalent radii ($r_1$ (Zn$^{2+}$) = 0.60 Å, $r_1$ (Cr$^{3+}$) = 0.62 Å, $r_1$ (Pb$^{2+}$) = 0.98 Å and $R_c$ (Zn$^{2+}$) = 0.74 Å, $R_c$ (Cr$^{3+}$) = 0.76 Å, $R_c$ (Pb$^{2+}$) = 1.12 Å, respectively) [51].

Table 2. Structural parameters of the Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$ single crystals.

| Chemical Formula            | Lattice Parameter (Å) | Volume ($Å^3$) | Density Calc. (Mg/m$^3$) | Absorption Coeff. (mm$^{-1}$) | Goodness of Fit on F$^2$ | R Parameters |
|-----------------------------|-----------------------|----------------|--------------------------|------------------------------|--------------------------|--------------|
|                             |                       |                |                          |                              |                          | $R_1$        | $wR_2$       |
| Zn$_{0.94}$Pb$_{0.06}$Cr$_2$Se$_4$ | 10.4910(3)           | 1154.65(2)    | 5.682                    | 32.837                       | 1.150                    | 0.0223       | 0.0662       |
| Zn$_{0.92}$Pb$_{0.08}$Cr$_2$Se$_4$ | 10.4933(2)           | 1155.41(3)    | 5.689                    | 32.883                       | 1.205                    | 0.0333       | 0.1114       |
| Zn$_{0.92}$Pb$_{0.08}$Cr$_2$Se$_4$ | 10.4946(4)           | 1155.84(1)    | 5.709                    | 32.856                       | 1.175                    | 0.0264       | 0.0839       |
| Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ | 10.4954(2)           | 1156.10(2)    | 5.757                    | 33.841                       | 1.196                    | 0.0333       | 0.1114       |
| Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ | 10.4959(1)           | 1156.27(3)    | 5.772                    | 33.852                       | 1.191                    | 0.0311       | 0.1012       |

Table 3. Atomic coordinates and equivalent isotropic displacement parameters of the Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$ single crystals. The Wyckoff positions of the atoms in the spinel structure are: Zn in 8 b (3/8, 3/8, 3/8); Cr/Ta in 16 c ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$); and Se in 32 e (x, x, x). $U_{eq}$ is defined as one-third of the orthogonalized Uij tensor trace.

| Spinel | Anion Parameter $u$ | Site Occupation (A) | Site Occupation (B) | Zn/Pb | $U_{iso}$ (Å$^2$) |
|--------|---------------------|---------------------|---------------------|-------|-------------------|
|        |                     |                     |                     |       | 10$^3$            |
| (Zn$_{0.94}$Pb$_{0.06}$)[Cr$_2$]Se$_4$ | 0.2595(1)          | 0.94(1):0.06(1)    | 1.0                 | 13(1) | 7(1)              |
| (Zn$_{0.92}$Pb$_{0.07}$)[Cr$_2$]Se$_4$ | 0.2595(1)          | 0.92(2):0.07(1)    | 1.0                 | 14(1) | 6(1)              |
| (Zn$_{0.92}$Pb$_{0.08}$)[Cr$_2$]Se$_4$ | 0.2595(1)          | 0.92(1):0.09(1)    | 1.0                 | 13(1) | 7(1)              |
| (Zn$_{0.88}$Pb$_{0.11}$)[Cr$_2$]Se$_4$ | 0.2595(1)          | 0.89(2):0.11(2)    | 1.0                 | 14(1) | 5(1)              |
| (Zn$_{0.88}$Pb$_{0.12}$)[Cr$_2$]Se$_4$ | 0.2595(1)          | 0.87(1):0.13(2)    | 1.0                 | 14(1) | 5(1)              |

The structural study confirmed the chemical composition obtained from SEM. The general formula of obtained single crystals can be described as Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$. The Pb ions substituted the Zn ones. The single crystals crystallised in a cubic system with space group $Fd-3m$ (No. 227, $Z = 8$). The lattice parameters of the obtained single crystals are slightly larger than pure ZnCr$_2$Se$_4$ ($a = 10.489$ Å) and enhanced with the increase in lead content (Table 2). The increase in lattice parameters is connected with the difference in ionic radii between Zn$^{2+}$ and Pb$^{2+}$ (Figure 5).
The positional parameter of Se ($u$) is a measure of the anion sublattice distortion from the cubic-close packing. The value of $u$ is the same for all obtained single crystals. Its value increases slightly compared to the ideal value of $u = 0.250$ (Table 3). The admixture of lead does not significantly affect the $u$-value. The same is observed in the metal–metal and metal–selenium distances (Table 4), where the differences are insignificant [22]. The structure refinement parameters, the selected bond distances, and angles are shown in Tables 3 and 4.

Table 4. Selected interatomic distances (Å) and bond angles (deg) of the Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$ spinel single crystals.

| Spinel                  | Bond Distances | Bond Angles       |
|-------------------------|----------------|-------------------|
|                         | Zn/Pb–Se       | Cr-Se             | Se–Zn/Pb–Se       | Se–Cr–Se       |
| $(Zn_{0.94}Pb_{0.06})[Cr_2]Se_4$ | 2.4451(5)      | 2.5282(3)         | 109.5(0) × 6      | 180.0(0) × 3   |
|                         |                |                   |                   | 94.61(13) × 6  |
|                         |                |                   |                   | 85.39(13) × 6  |
| $(Zn_{0.92}Pb_{0.07})[Cr_2]Se_4$ | 2.4442(7)      | 2.5269(4)         | 109.5(0) × 6      | 180.0(0) × 3   |
|                         |                |                   |                   | 94.61(2) × 6   |
|                         |                |                   |                   | 85.39(2) × 6   |
| $(Zn_{0.92}Pb_{0.08})[Cr_2]Se_4$ | 2.4453(5)      | 2.5274(3)         | 109.5(0) × 6      | 180.0(0) × 3   |
|                         |                |                   |                   | 94.62(14) × 6  |
|                         |                |                   |                   | 85.38(14) × 6  |
| $(Zn_{0.88}Pb_{0.11})[Cr_2]Se_4$ | 2.4453(8)      | 2.5279(4)         | 109.5(0) × 6      | 180.0(0) × 3   |
|                         |                |                   |                   | 94.62(2) × 6   |
|                         |                |                   |                   | 82.38(2) × 6   |
| $(Zn_{0.88}Pb_{0.12})[Cr_2]Se_4$ | 2.4453(7)      | 2.5280(4)         | 109.5(0) × 6      | 180.0(0) × 3   |
|                         |                |                   |                   | 94.61(2) × 6   |
|                         |                |                   |                   | 85.39(2) × 6   |

3.3. Electrical and Magnetic Properties

The results of the electrical measurements are shown in Figure 6 and Table 5, and the magnetic ones are in Figures 7–9 and Tables 5 and 6. Electrical conductivity measurements (Figure 6) showed semiconducting properties in the temperature range of 77–400 K for
all single crystals under study. Two regions of Arrhenius type electrical conductivity are visible: the extrinsic one with the activation energy of $E_a \approx 0.08$ eV below room temperature, independent of the Pb content in the sample, and the intrinsic one with $E_a$ increasing in the range of 0.138–0.315 eV above room temperature with increasing Pb content (Table 5).

![Figure 6](image-url). Electrical conductivity ($\ln\sigma$) vs. reciprocal temperature ($10^3/T$) for ZnCr$_2$Se$_4$ single crystals doped with Pb$^{2+}$ ions having contents of 0.06, 0.07, 0.09, 0.11, and 0.12.

Table 5. Magnetic parameters of Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$ single crystals recorded in an internal oscillating magnetic field $H_{ac} = 1$ Oe with an internal frequency $f = 120$ Hz and with a zero external static magnetic field: $C$ is the Curie constant; $T_N$ and $\theta$ are the Néel and Curie–Weiss temperatures, respectively; $\mu_{\text{eff}}$ is the effective magnetic moment; $J_1$ and $J_2$ are the super-exchange integrals for the first two coordination spheres. $H_{c1}$ and $H_{c2}$ are the critical fields measured at the static magnetic field up to 70 kOe. $E_a$ is the energy activation measured in the temperature range of 300–400 K. Experimental data for the ZnCr$_2$Se$_4$ matrix were taken from Refs. [1,21,22,31] for comparison.

| Spinel                  | $C$ (emu·K/mol) | $T_N$ (K) | $\theta$ (K) | $\mu_{\text{eff}}$ (µB/f.u.) | $M_{\text{S(OKL)}}$ (µB/f.u.) | $J_1$ (K) | $J_2$ (K) | $H_{c1}$ (kOe) | $H_{c2}$ (kOe) | $E_a$ (eV) |
|------------------------|----------------|-----------|--------------|-------------------------------|-------------------------------|-----------|-----------|----------------|----------------|-----------|
| ZnCr$_2$Se$_4$         | 4.082          | 21        | 90           | 5.714                         | 6.0                           | −1.65     | 1.28      | 10.0           | 65.0           | 0.135     |
| Zn$_{0.94}$Pb$_{0.06}$Cr$_2$Se$_4$ | 5.477          | 22        | 74           | 6.618                         | 5.325                         | −2.07     | 1.17      | 12.0           | 55.0           | 0.138     |
| Zn$_{0.92}$Pb$_{0.07}$Cr$_2$Se$_4$ | 5.568          | 22        | 77           | 6.673                         | 5.964                         | −1.95     | 1.23      | 12.0           | 56.0           | 0.161     |
| Zn$_{0.92}$Pb$_{0.07}$Cr$_2$Se$_4$ | 4.727          | 22        | 81           | 6.149                         | 5.960                         | −2.02     | 1.19      | 12.0           | 61.0           | 0.146     |
| Zn$_{0.90}$Pb$_{0.11}$Cr$_2$Se$_4$ | 5.768          | 22        | 83           | 6.792                         | 5.486                         | −1.92     | 1.24      | 12.0           | 55.0           | 0.177     |
| Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ | 5.898          | 22        | 84           | 6.868                         | 5.251                         | −1.90     | 1.25      | 12.0           | 57.0           | 0.315     |
Figure 7. Ac magnetic susceptibility $\chi_{ac}$ and its reciprocal $1/\chi_{ac}$ vs. temperature $T$ recorded at internal oscillating magnetic field $H_{ac} = 1$ Oe with internal frequency $f = 120$ Hz for the ZnCr$_2$Se$_4$ single crystals doped with Pb$^{2+}$ ions having contents of 0.06 (a), 0.07 (b), 0.09 (c), 0.11 (d), and 0.12 (e). The solid (black) line, $(T-\theta)/C$, indicates a Curie–Weiss behaviour.
Figure 8. Magnetization $M$ vs. magnetic field $H$ at 2, 4, 10, 20, 40, 60, and 300 K for the ZnCr$_2$Se$_4$ single crystals doped with Pb$^{2+}$ ions having contents of 0.06 (a), 0.07 (b), 0.09 (c), 0.11 (d), and 0.12 (e). The $M(H)$ isotherms recorded at 2 K with arrows denoting the first ($H_{c1}$) and second ($H_{c2}$) critical magnetic fields are shown in figure (f).
Figure 9. Ac magnetic susceptibility $\chi_{ac}$ vs. temperature $T$ recorded at internal oscillating magnetic field $H_{ac} = 1$ Oe with internal frequency $f = 120$ Hz for the ZnCr$_2$Se$_4$ single crystals doped with Pb$^{2+}$ ions having contents of 0.06 (a), 0.07 (b), 0.09 (c), 0.11 (d), and 0.12 (e) taken at external magnetic fields $H_{dc} = 0, 10, 20, 30, 40, \text{and} 50$ kOe. Vertical arrows indicate the Néel $T_N$ and $T_m$ temperatures, and horizontal ones indicate the shift of $T_N$ and $T_m$ with increasing magnetic field $H_{dc}$. 
Table 6. Magnetic parameters of the Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$ single crystals recorded in an internal oscillating magnetic field $H_{ac} = 1$ Oe with an internal frequency $f = 120$ Hz and taken at external static magnetic fields $H_{dc} = 0, 10, 20, 30, 40,$ and $50$ kOe: $C$ is the Curie constant; $T_N$, $\theta$, and $T_m$ are the Néel, Curie-Weiss, and the spin fluctuation temperatures, respectively; $\mu_{\text{eff}}$ is the effective magnetic moment; and $J_1$ and $J_2$ are the super-exchange integrals for the first two coordination spheres.

| Spinel            | $H_{dc}$ (kOe) | $C$ (emu K/mol) | $T_N$ (K) | $\theta$ (K) | $T_m$ (K) | $\mu_{\text{eff}}$ ($\mu_B$/f.u.) | $J_1$ (K) | $J_2$ (K) |
|-------------------|----------------|-----------------|-----------|---------------|-----------|-----------------------------------|-----------|-----------|
| Zn$_{0.94}$Pb$_{0.06}$Cr$_2$Se$_4$ | 0              | 5.477           | 22        | 74            | -         | 6.618                             | -2.07     | 1.17      |
|                   | 10             | 4.211           | 22        | 76            | -         | 5.803                             | -1.73     | 1.13      |
|                   | 20             | 4.086           | 18        | 79            | -         | 5.716                             | -1.38     | 1.11      |
|                   | 30             | 3.986           | 16        | 82            | -         | 5.646                             | -1.03     | 1.08      |
|                   | 40             | 3.948           | 12        | 95            | 31.5      | 5.619                             | 0.22      | 1.09      |
|                   | 50             | 3.863           | 6         | 108           | 46        | 5.558                             | 0.90      | 1.05      |
| Zn$_{0.92}$Pb$_{0.08}$Cr$_2$Se$_4$ | 0              | 5.568           | 22        | 77            | -         | 6.673                             | -1.95     | 1.23      |
|                   | 10             | 4.182           | 20        | 78            | -         | 5.783                             | -1.6      | 1.18      |
|                   | 20             | 4.102           | 19        | 81            | -         | 5.728                             | -1.45     | 1.18      |
|                   | 30             | 4.003           | 16        | 84            | -         | 5.658                             | -0.9      | 1.11      |
|                   | 40             | 3.988           | 12        | 96            | 33        | 5.648                             | -0.18     | 1.11      |
|                   | 50             | 3.976           | 7         | 99            | 44        | 5.639                             | 0.60      | 1.00      |
| Zn$_{0.92}$Pb$_{0.09}$Cr$_2$Se$_4$ | 0              | 4.727           | 22        | 81            | -         | 6.149                             | -2.02     | 1.19      |
|                   | 10             | 3.922           | 21        | 82            | -         | 5.601                             | -1.85     | 1.18      |
|                   | 20             | 3.711           | 20        | 84            | -         | 5.448                             | -1.65     | 1.17      |
|                   | 30             | 3.681           | 16        | 85            | -         | 5.426                             | -1.00     | 1.10      |
|                   | 40             | 3.602           | 12        | 97            | 33.5      | 5.367                             | -0.20     | 1.10      |
|                   | 50             | 3.639           | 6         | 108           | 46        | 5.369                             | 0.90      | 1.05      |
| Zn$_{0.89}$Pb$_{0.11}$Cr$_2$Se$_4$ | 0              | 5.768           | 22        | 83            | -         | 6.792                             | -1.92     | 1.24      |
|                   | 10             | 4.293           | 20        | 84            | -         | 5.859                             | -1.60     | 1.20      |
|                   | 20             | 4.182           | 19        | 85            | -         | 5.783                             | -1.4      | 1.18      |
|                   | 30             | 4.101           | 16        | 86            | -         | 5.727                             | -0.97     | 1.12      |
|                   | 40             | 4.056           | 12        | 91            | 34        | 5.695                             | -0.28     | 1.06      |
|                   | 50             | 4.002           | 6         | 97            | 48        | 5.657                             | 0.72      | 0.96      |
| Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$ | 0              | 5.898           | 22        | 84            | -         | 6.868                             | -1.90     | 1.25      |
|                   | 10             | 3.794           | 20        | 86            | -         | 5.508                             | -1.57     | 1.22      |
|                   | 20             | 3.781           | 19        | 88            | -         | 5.499                             | -1.38     | 1.21      |
|                   | 30             | 3.762           | 16        | 90            | -         | 5.485                             | -0.90     | 1.15      |
|                   | 40             | 3.703           | 12        | 94            | 36        | 5.442                             | -0.23     | 1.08      |
|                   | 50             | 3.689           | 6         | 98            | 48        | 5.432                             | 0.73      | 0.97      |

The increase in activation energy with the increase in lead content may be caused by the appearance of cationic vacancies (acting as double acceptors) because the radius of Pb$^{2+}$ ions is much larger than that of Zn$^{2+}$ ones [51]. It may result in acceptor vacancy levels in the energy gap. The activation energies mentioned above correlate well with $E_a$ for the matrix [31] and with its admixtures, such as tin [35], tantalum [37], and dysprosium [22].

The temperature dependencies of ac magnetic susceptibility $\chi_{ac}$, recorded in an internal oscillating magnetic field $H_{ac} = 1$ Oe with an internal frequency $f = 120$ Hz and with a zero external static magnetic field (Figure 7a–e), show AFM order with the Néel temperature $T_N = 22$ K and the positive Curie–Weiss temperature ($\theta$) slightly changing from 74 K to 84 K as the Pb content increases (Table 5).

The $\theta$ values are much lower than the literature data published in [21,22] and slightly lower than in [1], where $\theta$ is equal to 115 K and 90 K, respectively. Thus, only the $T_N$ temperature values are close to this temperature’s values for the ZnCr$_2$Se$_4$ matrix [1,21,22]. It means that the long-range AFM interactions are slightly more substantial. In contrast, the short-range FM ones are somewhat weaker in the sample containing Pb, which is confirmed by both the long bond lengths (Table 4) and the values of the $J_1$ and $J_2$ super-exchange integrals for the first two coordination spheres (Table 5). A significant difference was
observed between the effective magnetic moment ($\mu_{\text{eff}}$) and the effective number of Bohr magnetons, $p_{\text{eff}} = 5.477$, i.e., the spin contribution to the magnetic moment for Cr$^{3+}$ ions per molecule $3d^3$ configuration. It may suggest that the orbital magnetic contribution has not been quenched at low amplitude, $H_{\text{ac}} = 1$ Oe, of the applied oscillating magnetic field.

The magnetisation measurements (Figure 8a–e) show that the magnetic saturation of the studied samples is close to the value of 6 $\mu_B$/f.u. for the matrix; the first critical field is kept constant at $H_{c1} = 12$ kOe, and the second critical field is around $H_{c2} = 57$ kOe (Table 5). The hysteresis loops have zero-field coercivity and zero remanences (Figure 8f).

The temperature dependencies of ac magnetic susceptibility $\chi_{\text{ac}}$, recorded in an internal oscillating magnetic field $H_{\text{ac}} = 1$ Oe with an internal frequency $f = 120$ Hz and taken at external static magnetic fields $H_{\text{dc}} = 0, 10, 20, 30, 40,$ and $50$ kOe, are shown in Figure 9a–e. With the increase in $H_{\text{dc}}$, we observed a shift of $T_N$ towards lower temperatures and of $\theta$ towards higher ones (Table 6).

A strong magnetic field weakens the AFM order and strengthens the FM one. Moreover, the Curie constant, $C$, and the effective moment $\mu_{\text{eff}}$, are close to the values typical for a chromium ion per molecule. For $H_{\text{dc}} = 50$ kOe, the $J_1$ super-exchange integral for the first coordination sphere changes the sign from negative to positive, while the $J_2$ integral remains positive (Table 6). It means that the short-range FM interaction extends over the entire temperature range. The $\chi_{\text{ac}}(T)$ curves above $T_N$ in the paramagnetic region show characteristic wide maxima at $T_m = 32$–36 and 44–48 K in the fields $H_{\text{dc}} = 40$ and 50 kOe, respectively. These broad maxima of ac magnetic susceptibility may be due to the spin fluctuations that occur due to the amplification of short-range FM interactions by a static magnetic field, which is opposed by the thermal energy $kT$. Similar maxima were found in the ZnCr$_2$Se$_4$ matrix doped with Al [28], Ce, Ga, and In [33].

### 3.4. Specific Heat Studies

In Figure 10, the points represent the specific heat measured for samples with the formulae: Zn$_{0.92}$Pb$_{0.07}$Cr$_2$Se$_4$, Zn$_{0.92}$Pb$_{0.09}$Cr$_2$Se$_4$, Zn$_{0.89}$Pb$_{0.11}$Cr$_2$Se$_4$, and Zn$_{0.88}$Pb$_{0.12}$Cr$_2$Se$_4$.

![Figure 10. Specific heat, C, as a function of temperature T, measured for the Zn$_{1-x}$Pb$_x$Cr$_2$Se$_4$ single crystals (x = 0.07, 0.09, 0.11, and 0.12) at zero magnetic field (main figure). The dashed lines show the Debye model fit experimental data for T > 40 K. The upper inset shows how the magnetic peak is affected by Pb substitution. The lower inset shows how the magnetic transition temperature is affected by the magnetic field for the Zn$_{0.92}$Pb$_{0.07}$Cr$_2$Se$_4$ sample. Note that the temperature scales on the lower and upper inset are not the same. Hence, the peaks in the upper inset appear much broader than in the lower inset or the main figure.](image-url)

We see that the Debye model fits the experimental data well for all the samples, with the Debye temperatures obtained from the fits 163–177 K, with no apparent dependence of Debye temperature on the Pb concentration. The number of atoms obtained from the
fit lies within 7.2–9.5 for the investigated samples, without clear dependence on the Pb concentration. It can be explained by the fact that the change in sample composition is minute, and the changes in Zn concentration accompany the changes in Pb concentration. The upper inset of Figure 10 shows the specific heat in a narrow region around the magnetic ordering temperature. The sample $\text{Zn}_{0.92}\text{Pb}_{0.09}\text{Cr}_2\text{Se}_4$ exhibits quite a sharp peak in the vicinity of magnetic transition, whereas the remaining compositions show a broader two-peak-like structure. This is most likely caused by the disorder induced by the Pb substitution and the lack of full site occupancy of the Zn site. The bottom inset of Figure 10 shows the shift of the magnetic transition with the increase in magnetic field for the $\text{Zn}_{0.92}\text{Pb}_{0.07}\text{Cr}_2\text{Se}_4$ sample, which is a clear manifestation of antiferromagnetic order.

We also measured the resistivity for the $\text{Zn}_{0.88}\text{Pb}_{0.12}\text{Cr}_2\text{Se}_4$ sample (the sample with the highest Pb concentration) with the resistivity option in the PPMS instrument (Figure 11). Below 120 K, the resistivity exceeded the range of the instrument. However, in the 120–300 K range, the resistivity can be well-fitted with an activation law $\rho = \rho_0 \exp(\Delta/kT)$ ($\rho_0$—resistivity at 273.15 K), where for an indirect bandgap, we obtained $\Delta \approx 0.88$ eV. The inset shows the resistivity measured vs. magnetic field at room temperature.

![Figure 11. The resistivity of the $\text{Zn}_{0.88}\text{Pb}_{0.12}\text{Cr}_2\text{Se}_4$ single crystal measured vs. temperature (central Figure) and vs. field at $T = 300$ K (inset). The $\text{Zn}_{0.88}\text{Pb}_{0.12}\text{Cr}_2\text{Se}_4$ sample was tiny. Hence, we do not provide the absolute value of the resistivity.](image)

The magnetoresistivity is positive and almost linear with the magnetic field. It is also relatively small, below 2% for 9 T.

3.5. Thermal Analysis

The thermal analysis examined two crystals of $\text{Zn}_{1-x}\text{Pb}_x\text{Cr}_2\text{Se}_4$ containing minimum (0.06) and maximum (0.12) lead amounts. The DSC and TG curves are depicted in Figure 12.

The shape of the DSC curves is similar to pure $\text{ZnCr}_2\text{Se}_4$. For the sample $\text{Zn}_{0.94}\text{Pb}_{0.06}\text{Cr}_2\text{Se}_4$, two small endothermic peaks are observed at 711 °C and 733 °C. The observed peaks are in a similar position close to pure $\text{ZnCr}_2\text{Se}_4$ (755 °C) [44]. These peaks indicate that the melting process of the sample starts at about 711 °C. The peak confirms it on the DTG curve. However, the sample $\text{Zn}_{0.88}\text{Pb}_{0.12}\text{Cr}_2\text{Se}_4$ lacks typical endothermic peaks. On the TG curves for both samples, a few percent increase in weight is visible in the first step. This phenomenon can indicate that the investigated sample absorbs an inert gas during the heating or solid-state–gas reaction. The mass loss is observed with increasing temperature on the DTG curve. It is an endothermic reaction, as indicated by the downward deflection of the DSC curve. The partial destruction of investigated samples takes place at about 1300 °C. It suggests that the samples doped with Pb are thermally more stable than pure $\text{ZnCr}_2\text{Se}_4$. 
Figure 12. DSC/TG curves for $\text{Zn}_{0.94}\text{Pb}_{0.06}\text{Cr}_2\text{Se}_4$ (a) and $\text{Zn}_{0.88}\text{Pb}_{0.12}\text{Cr}_2\text{Se}_4$ (b) single crystals.

4. Conclusions

In conclusion, we have demonstrated the family of $\text{Zn}_{1-x}\text{Pb}_x\text{Cr}_2\text{Se}_4$ ($x = 0.06, 0.07, 0.09, 0.11, 0.12$) spinel single crystals showing semiconducting and AFM behaviour. These single crystals were successfully obtained using chemical vapour transport. The technology of crystal growth was based on thermodynamic calculations. XRD analysis showed that these crystals possess a cubic structure (SG: $Fd\bar{3}m$). Thermal analysis showed that the single crystals under study are thermally stable up to $1300^\circ$C.

With the increase in the external magnetic field, a shift of $T_N$ and the specific heat peak towards lower temperatures and $\theta$ towards higher ones was observed, as well as a strong weakening of long-range AFM interactions visible in the reduction of the super-exchange integral for the first coordination sphere and the appearance of spin fluctuations in the paramagnetic region, visible in magnetic fields of 40 and 50 kOe. Below $T_N$, the magnetic field dependence of magnetisation, $M(H)$, showed two peculiarities at critical fields $H_{c1} = 12$ and $H_{c2} = 57$ kOe and a change of the sign of the $J_1$-integral from negative to positive at $H_{dc} = 50$ kOe, which causes the short-range FM interaction to extend over the entire temperature range. Finally, we can conclude that doped chalcogenide spinels are suitable materials for application in many technological areas, such as magnetic materials for capacitors, transformers, or components in electronic products.

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References

1. Hemberger, J.; von Nidda, H.-A.K.; Tsurkan, V.; Loidl, A. Large Magnetostriiction and Negative Thermal Expansion in the Frustrated Antiferromagnet ZnCr$_2$Se$_4$. *Phys. Rev. Lett.* 2007, 98, 147203. [CrossRef] [PubMed]

2. Kondo, S.; Johnston, D.C.; Swenson, C.A.; Borsa, F.; Mahajan, A.V.; Miller, L.L.; Gu, T.; Goldman, A.I.; Maple, M.B.; Gajewski, D.A.; et al. LiV$_2$O$_4$: A Heavy Fermion Transition Metal Oxide. *Phys. Rev. Lett.* 1997, 78, 3729–3732. [CrossRef]

3. Krimmel, A.; Loidl, A.; Klemm, M.; Horn, S.; Schobes, H. Dramatic Change of the Magnetic Response in LiV$_2$O$_4$: Possible Heavy Fermion to Itinerant-$d$-Metal Transition. *Phys. Rev. Lett.* 1999, 82, 2919–2922. [CrossRef]

4. Lee, S.-H.; Broholm, C.; Rackliff, W.; Gasparovic, G.; Huang, Q.; Kim, T.H.; Cheong, S.W. Emergent excitations in a geometrically frustrated magnet. *Nature* 2002, 418, 856–858. [CrossRef] [PubMed]

5. Radaelli, P.; Horibe, Y.; Gutmann, M.J.; Ishibashi, H.; Chen, C.H.; Ibberson, R.M.; Koyama, Y.; Hor, Y.S.; Kiryukhin, V.; Cheong, S.W. Formation of isomorphic $\text{Ir}^{3+}$ and $\text{Ir}^{4+}$ octamers and spin dimerisation in the spinel $\text{CuIr}_2\text{S}_4$. *Nature* 2002, 416, 155–158. [CrossRef] [PubMed]

6. Schmidt, M.; Rackliff, W.; Radaelli, P.G.; Refson, K.; Harrison, N.M.; Cheong, S.W. Spin Singlet Formation in MgTi$_2$O$_4$. *Phys. Rev. Lett.* 1994, 72, 262–265. [CrossRef] [PubMed]

7. Fritsch, V.; Hemberger, J.; Bütting, N.; Scheidt, E.-W.; Krug von Nidda, H.-A.; Tsurkan, V. Spin and Orbital Frustration in MnSe$_2$S$_2$ and FeSe$_2$S$_2$. *Phys. Rev. Lett.* 2004, 92, 116401. [CrossRef] [PubMed]

8. Krimmel, A.; Mücksch, M.; Tsurkan, V.; Koza, M.M.; Mutka, H.; Loidl, A. Vibronic and Magnetic Excitations in the Spin-Orbital Liquid State of FeSe$_2$S$_2$. *Phys. Rev. Lett.* 2005, 94, 237402. [CrossRef]

9. Fichtl, R.; Tsurkan, V.; Lunkenheimer, P.; Hemberger, J.; Fritsch, V.; Krug von Nidda, H.-A.; Scheidt, E.-W.; Loidl, A. Orbital Freezing and Orbital Glass State in FeCr$_2$S$_4$. *Phys. Rev. Lett.* 2005, 94, 027601. [CrossRef]

10. Hemberger, J.; Lunkenheimer, P.; Fichtl, R.; Krug von Nidda, H.-A.; Tsurkan, V.; Loidl, A. Relaxor ferroelectricity and colossal magnetocapacitance coupling in ferromagnetic CdCr$_2$S$_4$. *Nature* 2005, 434, 364–367. [CrossRef]

11. Weber, S.; Lunkenheimer, P.; Fichtl, R.; Hemberger, J.; Tsurkan, V.; Loidl, A. Colossal Magnetocapacitance and Colossal Magnetoresistance in HgCr$_2$S$_4$. *Phys. Rev. Lett.* 2006, 96, 157202. [CrossRef] [PubMed]

12. Yamazaki, Y.; Miyasaka, S.; Kaneko, Y.; He, J.-P.; Arima, T.; Tokura, Y. Magnetic Reversal of the Ferroelectric Polarisation in a Multiferroic Spinel Oxide. *Phys. Rev. Lett.* 2006, 96, 207204. [CrossRef] [PubMed]

13. Lee, S.-H.; Broholm, C.; Kim, T.H.; Rackliff, W.; Cheong, S.-W.; Kim, T.H.; Rackliff, W. Local Spin Resonance and Spin-Peierls-like Phase Transition in a Geometrically Frustrated Antiferromagnet. *Phys. Rev. Lett.* 2000, 84, 3718. [CrossRef]

14. Tchernyshyov, O.; Moessner, R.; Sondhi, S.L. Order by Distortion and String Modes in Pyrochlore Antiferromagnets. *Phys. Rev. Lett.* 2002, 88, 067205. [CrossRef] [PubMed]

15. Yamashita, Y.; Ueda, K. Spin-Driven Jahn-Teller Distortion in a Pyrochlore System. *Phys. Rev. Lett.* 2000, 85, 4960. [CrossRef] [PubMed]

16. Hemberger, J.; Rudolf, T.; Krug von Nidda, H.-A.; Mayr, F.; Pimenov, A.; Tsurkan, V.; Loidl, A. Spin-Driven Phonon Splitting in Bond-Frustrated ZnCr$_2$S$_4$. *Phys. Rev. Lett.* 2007, 97, 087207. [CrossRef]

17. Groń, T.; Duda, H.; Warczewski, J. 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$_{2/3}$). *Phys. Rev. B* 1990, 41, 12424–12431. [CrossRef]

18. Groń, T. Influence of vacancies and mixed valence on the transport processes in solid solutions with the spinel structure. *Philos. Mag. B* 1994, 70, 121–132. [CrossRef]

19. Groń, T.; Wolff, J.; Hehenkamp, T.; Bärner, K.; Okońska-Kozlowska, I.; Jendrzejewska, I.; Malicka, E. Positron annihilation studies in single and polycrystals of Zn$_{1-x}$Cu$_x$Cr$_2$Se$_4$ spinel series. *Radiat. Eff. Defects Solids* 1996, 139, 97–107. [CrossRef]

20. Parker, D.R.; Green, M.A.; Bramwell, S.T.; Wills, A.S.; Gardner, J.S.; Neumann, D.A. Crossover from Positive to Negative Magnetoresistance in a Spinel. *J. Am. Chem. Soc.* 2004, 126, 2710–2711. [CrossRef]

21. Lotgering, F.K. Ferromagnetic interactions in sulphides, selenides and tellurides with spinel structure. In Proceedings of the International Conference on Magnetism, Nottingham, UK, 7–11 September 1964; Institute of Physics and the Physical Society London: London, UK, 1965; p. 533.

22. Plumier, R. Étude par diffraction de neutrons de l’antiferromagnétisme hélioidal du spinelle ZnCr$_2$Se$_4$ en présence d’un champ magnétique. *J. Phys.* 1966, 27, 213–219. [CrossRef]

23. Park, S.; Kwon, S.; Lee, S.; Khim, S.; Bhoi, D.; Park, C.B.; Kim, K.H. Interactions in the bond-frustrated helimagnet ZnCr$_2$Se$_4$ investigated by NMR. *Sci. Rep.* 2019, 9, 16627. [CrossRef] [PubMed]

24. Kleinberger, R.; de Kouchkovsky, C.R. Étude cristallographique à base de temperature du spinelle ZnCr$_2$Se$_4$. *Acad. Sci. Paris Ser. B* 1966, 262, 628–630.
25. Yokaiiya, F.; Krimmel, A.; Tsurkan, V.; Margioliak, I.; Thompson, P.; Bordallo, H.N.; Buchsteiner, A.; Stußer, N.; Argyriou, D.N.; Loidl, A. Spin-driven phase transitions in ZnCr2Se4 and ZnCr2S4 probed by high-resolution synchrotron X-ray and neutron powder diffraction. Phys. Rev. B 2009, 79, 064423. [CrossRef]

26. Malicka, E.; Groń, T.; Pacyna, A.W.; Maciżek, E.; Duda, H.; Pawelczyk, M.; Zawisza, B.; Sitko, R. Influence of temperature on the critical fields in ZnCr2-xAl2-xSe4 antiferromagnets. J. Alloys Compd. 2009, 480, 67–69. [CrossRef]

27. Groń, T.; Malicka, E.; Duda, H.; Pacyna, A.W.; Mydlarz, T.; Sitko, R.; Pawelczyk, M. Spin-glass-like behavior in Zn2-xCr4-xAl2Se4. J. Phys. Chem. Sol. 2009, 70, 1175–1180. [CrossRef]

28. Malicka, E.; Groń, T.; Ślebarski, A.; Pacyna, A.W.; Goraus, J.; Fijalkowski, M.; Heimann, J. Specific heat and magnetic susceptibility of single-crystaline Zn2-xCr2-xAl2Se4 (x = 0.15, 0.23). J. Phys. Chem. Sol. 2011, 72, 974–979. [CrossRef]

29. Groń, T.; Jendrzejewska, I.; Gołąbek, S.; Duda, H.; Krajewski, A.; Barśnik, K. The thermoelectric power of ferromagnetically ordered ZnCu2Cr2Se4 single crystals. Phys. B 2003, 327, 88–95. [CrossRef]

30. Mazur, S.; Groń, T.; Jendrzejewska, I. Influence of spin arrangement on thermopower in Zn2-xCu3-xCr4-xSe4 spinels. J. Alloys Compd. 2009, 480, 19–22. [CrossRef]

31. Okońska-Kołowska, I.; Lutz, H.D.; Groń, T.; Krok, J.; Mydlarz, T. Darstellung, elektrische und magnetische Eigenschaften von-Zn1-xGa0.667-xCr2-xSe4-Spinell-Einkristallen. Mater. Res. Bull. 1984, 19, 1–5. [CrossRef]

32. Groń, T.; Duda, H.; Warczewski, J. Transport phenomena in the antiferromagnetic spinels Zn1-xGa2x/3Cr2Se4 (where 0.0 < x < 0.5). J. Magn. Magn. Mater. 1990, 83, 487–489. [CrossRef]

33. Malicka, E.; Groń, T.; Ślebarski, A.; Gagor, A.; Pacyna, A.W.; Sitko, R.; Goraus, J.; Mydlarz, T.; Heimann, J. Specific heat and magnetic susceptibility of single-crystaline Zn2-xCr2-xAl2Se4 spinels doped with Ga, In and Ce. Mater. Chem. Phys. 2011, 131, 142–150. [CrossRef]

34. Groń, T.; Kopryczok, J.; Okońska-Kołowska, I.; Warczewski, J. Seebeck effect in the antiferromagnetic single crystals of ZnCr2-x-InxSe4 (0.0 < x < 0.15). J. Magn. Magn. Mater. 1992, 111, 53–55. [CrossRef]

35. Jendrzejewska, I.; Groń, T.; Kusz, J.; Zielechower, M.; Maciżek, E.; Ślebarski, A.; Fijalkowski, M. Spin-glass-like behaviour in tin doped ZnCr2Se4 single crystals. J. Alloys Compd. 2015, 635, 238–244. [CrossRef]

36. Jendrzejewska, I.; Mroziński, J.; Groń, T.; Duda, H.; Zajdel, P.; Pacyna, A.W.; Maciżek, E.; Hanc, A. Effect of cation substitution on Fermi level of n-type Zn2-xSnxCr2-xSe4 spinels. J. Alloys Compd. 2009, 480, 63–66. [CrossRef]

37. Jendrzejewska, I.; Groń, T.; Kwapulinski, P.; Kusz, J.; Pietrasik, E.; Goryczka, T.; Sawicki, B.; Ślebarski, A.; Fijalkowski, M.; Jampilek, J.; et al. Study of the structure, magnetic, thermal and electrical characterisation of ZnCr2Se4:Ta single crystals obtained by chemical vapour transport. Materials 2021, 14, 2749. [CrossRef]

38. Jendrzejewska, I.; Groń, T.; Kniżek, K.; Pilch, M.; Ślebarski, A.; Goraus, J.; Zajdel, P.; Stoklosa, Z.; Pietrasik, E.; Goryczka, T.; et al. Preparation, structure and magnetic, electronic and thermal properties of Dy3+ doped ZnCr2Se4 with unique geometrical type spin-glass. J. Sol. State Chem. 2021, 298, 122114. [CrossRef]

39. Jendrzejewska, I.; Groń, T.; Maciżek, E.; Duda, H.; Kubisztal, M.; Ślebarski, A.; Pietrasik, E.; Fijalkowski, M. Specific heat and magnetic properties of single-crystaline Zn2-xDyxCr2-xSe4 spinels. J. Magn. Magn. Mater. 2016, 407, 122–128. [CrossRef]

40. Maciżek, E.; Karolus, M.; Kubisztal, M.; Jendrzejewska, I.; Sitko, R.; Groń, T.; Ślebarski, A.; Fijalkowski, M. Magnetic and specific heat properties of a new Gd-doped ZnCr2Se4. Mater. Chem. Phys. 2015, 168, 187–192. [CrossRef]

41. Jendrzejewska, I.; Groń, T.; Kusz, J.; Goraus, J.; Barsova, Z.; Pietrasik, E.; Czerwiński, J.; Goryczka, T.; Kubisztal, M. Growth, structure and physico-chemical properties of monoclinic ZnCr2Se4:Ho prepared by chemical vapour transport. J. Sol. State Chem. 2020, 281, 121024. [CrossRef]

42. Jendrzejewska, I.; Groń, T.; Goraus, J.; Pilch, M.; Pietrasik, E.; Barsova, Z.; Czerwiński, J.; Goryczka, T.; Witkowska-Kita, B.; Bienko, A.; et al. Synthesis and structural, magnetic, thermal and electronic properties of Mn-doped ZnCr2Se4. Mater. Chem. Phys. 2019, 238, 121901. [CrossRef]

43. Jendrzejewska, I.; Zajdel, P.; Heimann, J.; Krok-Kowalski, J.; Mydlarz, T.; Mrzigod, J. Influence of manganese on magnetic and electronic properties of ZnCr2-xSe4 single Crystals. Mater. Res. Bull. 2012, 47, 1881–1886. [CrossRef]

44. Jendrzejewska, I.; Groń, T.; Kusz, J.; Barsova, Z.; Pietrasik, E.; Goryczka, T.; Sawicki, B.; Ślebarski, A.; Fijalkowski, M.; Jampilek, J.; et al. Synthesis, crystal structure and characterization of monoclinic ZnCr2Se4 doped with neodymium. J. Sol. State Chem. 2020, 292, 121661. [CrossRef]

45. Jendrzejewska, I.; Waśkowska, A.; Mydlarz, T. Influence of nickel substitution on the cation distribution and magnetic properties of ZnCr2Se4. J. Alloys Compd. 2001, 327, 73–77. [CrossRef]

46. Lenz, M.; Gruehn, R. Developments in Measuring and Calculating Chemical Vapor Transport Phenomena Demonstrated on Cr, Mo, W and Their Compounds. Chem. Rev. 1997, 97, 2967–2994. [CrossRef]

47. Plies, V. Massenspektrometrische Untersuchungen der Gasphase über CrCl3 und CrCl3/Cl2. Z. Anorg. Allg. Chem. 1988, 556, 120–128. [CrossRef]

48. Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Cryst. 2015, C71, 3–8.

49. Morrish, A.H. Physical Principles of Magnetism; John Wiley & Sons, Inc.: New York, NY, USA, 1965.

50. Holland, W.E.; Brown, H.A. Application of the Weiss molecular field theory to the B-site spinel. Phys. Status Solidi 1972, 10, 249–253. [CrossRef]

51. Shannon, R.D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. Acta Cryst. 1976, A32, 751–767. [CrossRef]