Flux synthesis, crystal structures, and magnetic ordering of the rare-earth chromium(II) oxselenides $RE_2CrSe_2O_2$ ($RE = La-Nd$)

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ABSTRACT

The rare-earth chromium(II) oxyselenides $RE_2CrSe_2O_2$ ($RE = La-Nd$) have been synthesized in eutectic NaI/KI fluxes and their crystal structures were determined by single crystal and powder X-ray diffraction ($Pb_2HgCl_2O_2$ -type, $C2/m$, $Z = 2$). The magnetic structure of $La_2CrSe_2O_2$ has been solved and refined from neutron powder diffraction data. Main building blocks are chains of edge-sharing $CrSe_4O_2$ -octahedra linked together by two edge-sharing ORE_3Cr -tetrahedra forming infinite ribbons. The Jahn-Teller instability of divalent Cr^{2+} (d^4) leads to structural phase transitions at 200 K and 130 K in $La_2CrSe_2O_2$ and $Ce_2CrSe_2O_2$, respectively. $RE_2CrSe_2O_2$ are Curie-Weiss paramagnetic above $T_N \approx 14-17$ K. Neutron powder diffraction reveals antiferromagnetic ordering of the Cr^{2+} moments in $La_2CrSe_2O_2$ below $T_N = 12.7(3)$ K with an average ordered moment of $3.40(4) \mu_B/Cr^{2+}$ at 4 K, which was confirmed by muon spin rotation experiments.

KEYWORDS Oxyselenides; Chromium; Rare-Earth; Crystal Structure; Magnetism

INTRODUCTION

Since the discovery of superconductivity in rare-earth oxide iron pnictides and iron chalcogenides during the last decade, there is ongoing interest in uncovering new rare-earth oxide transition metal selenides. Recently, the series $RE_2TSe_2O_2$ ($RE = La, Ce$; $T = Cd, Fe, Mn, Zn$)¹⁻¹⁰ have been reported and their structures and physical properties have been studied. These compounds adopt a layered, $ZrCuSiAs$ -related structure with modulated transition metal selenide layers with a (3+1)-dimensional structure in the superspace group $Cmme(\alpha 0\frac{1}{2})0s0$.⁹ Further polymorphs exist with $T = Mn$ and Fe , respectively. In order to distinguish the polymorphs, we

extended the formulas by the *Pearson* letters. Beside the modulated compound *oC*- $\text{La}_2\text{MnSe}_2\text{O}_2$ ^{6,10}, there exist *oA*- $\text{La}_2\text{MnSe}_2\text{O}_2$ ² and *mC*- $\text{La}_2\text{MnSe}_2\text{O}_2$. *oA*- $\text{La}_2\text{MnSe}_2\text{O}_2$ consists of disordered MnSe_4 -tetrahedra and edge-sharing MnSe_4O_2 -octahedra, which are connected by infinite ribbons of edge-sharing OLa_4 - and OLa_3Mn -tetrahedra four tetrahedral units in width. Ordering of the manganese cations is observed at low temperature, leading to a primitive structure with space group *Pna*2₁ (*oP*- $\text{La}_2\text{MnSe}_2\text{O}_2$). *mC*- $\text{La}_2\text{MnSe}_2\text{O}_2$ crystallizes in the $\text{Pb}_2\text{HgCl}_2\text{O}_2$ structure type with edge-sharing, distorted MnSe_4O_2 -octahedra, linked together by two edge-sharing OLa_3Mn -tetrahedra. Beside *oC*- $\text{RE}_2\text{FeSe}_2\text{O}_2$ ($\text{RE} = \text{La}, \text{Ce}$)^{3,5} in the iron family, there exist *mC*- $\text{RE}_2\text{FeSe}_2\text{O}_2$ ($\text{RE} = \text{La}, \text{Ce}$)⁵, which are isostructural to the monoclinic manganese compound, as well as *oP*- $\text{La}_2\text{FeSe}_2\text{O}_2$ ² and *oA*- $\text{Ce}_2\text{FeSe}_2\text{O}_2$ ⁵, which adopt the low temperature and room temperature structure of the analogous manganese compound, respectively. Magnetic measurements of *mC*- $\text{La}_2\text{MnSe}_2\text{O}_2$, *mC*- $\text{La}_2\text{FeSe}_2\text{O}_2$ and *oA*- $\text{La}_2\text{MnSe}_2\text{O}_2$ indicate antiferromagnetic ordering of the transition metal moments at Néel temperatures of $\approx 15, 20$ and 27 K, respectively.^{2,5}

Surprisingly only few rare-earth chromium oxyselenide compounds are known to date, namely RECrSe_2O ($\text{RE} = \text{La}^{11}, \text{Ce}^{12}$) with trivalent Cr^{3+} . LaCrSe_2O is isostructural to orthorhombic LaCrS_2O . The structure consists of edge-sharing CrSe_5O -octahedra interconnected by two edge-sharing OLa_3Cr -tetrahedra forming infinite ribbons. Magnetic measurements revealed long range ferromagnetic exchange interactions. CeCrSe_2O crystallizes in the monoclinic CeCrS_2O structure type, space group *C2/m*. The structure resembles this of *mC*- $\text{RE}_2\text{TSe}_2\text{O}_2$ ($\text{RE} = \text{La}, \text{Ce}$; $\text{T} = \text{Fe}, \text{Mn}$) with the same building blocks but additional edge-sharing CrSe_6 -octahedra, which connect the CrSe_4O_2 -octahedra. In this paper, we present the crystallographic and magnetic structures of

$\text{La}_2\text{CrSe}_2\text{O}$ with chromium in the less common oxidation state Cr^{2+} together with isomorphous compounds $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{Ce-Nd}$).

EXPERIMENTAL

All starting materials (purity $\geq 99.8\%$) were handled in an argon-filled glove box (M. Braun, $p(\text{O}_2) \leq 1$ ppm, $p(\text{H}_2\text{O}) \leq 1$ ppm). Polycrystalline powder samples and single crystals of mC - $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{La-Nd}$) were prepared in the same way by the reaction of appropriate amounts of rare-earth oxide, freshly filed rare-earth metal, Cr and Se. (See Table S3 in the supporting information for exact atomic ratios.) The rare-earth oxides were heated to 1273 K prior to use. The starting materials (0.20 g) were mixed intimately and sandwiched in alumina crucibles between 0.50 g of an eutectic mixture of NaI/KI (mass ratio 0.6:0.4, dried in dynamic vacuum at 673 K). In addition, a polycrystalline sample (3×1 g) of $\text{La}_2\text{CrSe}_2\text{O}_2$ was synthesized for neutron diffraction experiments. The crucibles were sealed in argon filled silica tubes and heated to 1173 K with a 50 h dwell time, followed by slow cooling to 873 K. The crucibles were quenched in air from 873 K. The reaction mixtures were then washed with deionized water and ethanol and dried in vacuum. The procedure (heating with flux material and washing) was repeated once in order to increase the purity of the samples. The resulting samples were black powder (purity > 95 wt% according to Rietveld refinements) and black, rod-like single crystals.

Single crystal X-ray diffraction data was collected at 300 K with a Bruker D8 QUEST (fixed- χ goniometer, Mo- $\text{K}\alpha$, $\text{I}\mu\text{S}$ with HE-LIOS multi-layer optics, PHOTON 100 detector). Reflection intensity integration, data reduction, and multi-scan absorption correction were done with APEX2¹³ and SADABS¹⁴. The structures were solved with Jana2006¹⁵.

X-ray powder diffraction patterns were recorded between 10 and 300 K with a Huber G670 diffractometer (Cu- $K_{\alpha 1}$ or Co- $K_{\alpha 1}$ radiation, Ge-monochromator, closed-cycle helium cryostat). For Rietveld refinements of the data the TOPAS¹⁶ package was used with spherical harmonic functions to describe the preferred orientation of the crystallites. Therefore the phase fractions from Rietveld refinements using X-ray powder diffraction may not be reliable. Thus, the purity of $\text{La}_2\text{CrSe}_2\text{O}_2$ was double-checked from refinements using neutron powder diffraction data.

Neutron powder diffraction measurements of $\text{La}_2\text{CrSe}_2\text{O}_2$ at 4, 20 and 300 K were performed at SPODI (FRM II, Garching)¹⁷ with a wavelength of 0.1548 nm. Rietveld refinements of the neutron data was done with FullProf¹⁸.

Magnetization isotherms and susceptibility measurements were performed with a MPMS-XL SQUID magnetometer (Quantum Design Inc.). Magnetization isotherms at higher fields ($B = \pm 9$ T) were measured with a Vibrating Sample Magnetometer unit (VSM) in a Quantum Design Physical-Property-Measurement-System (PPMS).

The μSR measurements were performed using the GPS spectrometer located at the πM3 beamline of the Swiss Muon Source at the Paul Scherrer Institut, Switzerland in a temperature range from 1.6 K to 40 K using a He flow cryostat. Transverse field μSR data were taken in a field of 50 Oe applied perpendicular to the initial muon spin. The data were analyzed using the free MUSRFIT package¹⁹.

RESULTS AND DISCUSSION

Synthesis and Crystal Structure

Single crystals of $\text{La}_2\text{CrSe}_2\text{O}_2$ were first obtained by the attempt to prepare a potential ‘ $\text{La}_3\text{CrSe}_3\text{O}_3$ ’. However, energy dispersive X-ray spectroscopy revealed the formation of a mixture of LaCrSe_2O and $\text{La}_2\text{CrSe}_2\text{O}_2$, which both crystallize as black needles. Almost phase pure samples of $\text{La}_2\text{CrSe}_2\text{O}_2$ have been obtained from the reaction of appropriate amounts of La_2O_3 , La, Cr and Se in a NaI/KI-flux synthesis. In addition, polycrystalline samples of $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{Ce–Nd}$) have been prepared in the same way as for $\text{La}_2\text{CrSe}_2\text{O}_2$.

Single-crystal X-ray diffraction experiments of $\text{La}_2\text{CrSe}_2\text{O}_2$ and powder X-ray diffraction experiments of $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{La–Nd}$) revealed that the new compounds crystallize in the $\text{Pb}_2\text{HgCl}_2\text{O}_2$ structure type in space group $C2/m$ (No. 12), equal to $mC\text{-RE}_2\text{TSe}_2\text{O}_2$ ($\text{RE} = \text{La, Ce; } T = \text{Mn, Fe}$)⁵. Relevant crystallographic data of $\text{La}_2\text{CrSe}_2\text{O}_2$ is compiled in Table S1 in the supplementary information. Further structural discussion is based on powder X-ray and neutron diffraction data of the isostructural compounds $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{La–Nd}$).

Rietveld refinements of $\text{La}_2\text{CrSe}_2\text{O}_2$ (Fig. 1), $\text{Ce}_2\text{CrSe}_2\text{O}_2$ and $\text{Pr}_2\text{CrSe}_2\text{O}_2$ (Fig. S1–2) revealed a small impurity of $\approx 1\text{--}4\%$ RE_2SeO_2 ($\text{RE} = \text{La–Pr}$), respectively. In contrast, only $\approx 10\%$ of the desired product was obtained for $\text{Nd}_2\text{CrSe}_2\text{O}_2$, while large amounts of NdCrSe_2O and Nd_2SeO_2 have been formed. We could not prepare heavier rare-earth analogues under these conditions.

Figure 1. Neutron powder diffraction pattern of $\text{La}_2\text{CrSe}_2\text{O}_2$ (blue) with Rietveld fit (red) and difference plot (gray) at 300 K.

The crystal structure of the new compounds is closely related to that of CeCrSe_2O as can be seen in Figure 2. It consists of chains of edge-sharing, distorted CrSe_4O_2 -octahedra parallel to the b -axis, linked together by two edge-sharing ORE_3Cr -tetrahedra forming infinite ribbons along b . The rare-earth metal is in a bicapped trigonal prism of five selenium and three oxygen atoms. These building blocks can be found again in CeCrSe_2O , but additional chains of edge-sharing CrSe_6 -octahedra exist along b , which interconnect the CrSe_4O_2 -octahedra and extend the rare-earth metal coordination sphere to a tricapped trigonal prism with one additional selenium atom. Single crystal X-ray data of $\text{La}_2\text{CrSe}_2\text{O}_2$ revealed that the displacement ellipsoid of the chromium atom exhibits the same oblate spheroid shape in direction of the selenium atoms that was already observed for the transition metal sites in $m\text{C-La}_2\text{FeSe}_2\text{O}_2^5$, $m\text{C-La}_2\text{MnSe}_2\text{O}_2$ and $\text{RE}_4\text{TiSe}_4\text{O}_4$ ($\text{RE} = \text{Sm-Er, Y}$)²⁰. This may indicate a dynamic displacement of the Cr^{2+} atoms in the distorted CrSe_4O_2 -octahedra. A comparison of the structural parameters obtained from X-ray powder data of $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{La-Nd}$) is given in Table 1.

Figure 2. Illustration of the crystal structures of (a+b) $RE_2CrSe_2O_2$ ($RE = La-Nd$) and (c) $CeCrSe_2O$ along b . Chains of edge-sharing $CrSe_4O_2$ - and $CrSe_6$ -octahedra in green, ORE_3Cr edge-sharing tetrahedral ribbons in blue. Ellipsoids in (a) represent 99 % probability.

Table 1. Rietveld refinement data of $RE_2CrSe_2O_2$ ($RE = La-Nd$) in space group $C2/m$.

	$La_2CrSe_2O_2$	$Ce_2CrSe_2O_2$	$Pr_2CrSe_2O_2$	$Nd_2CrSe_2O_2$
a in Å	11.536(1)	11.436(1)	11.414(1)	11.372(1)
b in Å	3.9682(1)	3.9314(1)	3.9101(1)	3.8782(1)
c in Å	7.1800(2)	7.1193(1)	7.0949(1)	7.0630(1)
β in °	121.617(1)	121.856(1)	121.800(1)	121.639(5)
Volume in Å ³	279.905(9)	271.864(3)	269.117(7)	265.21(4)
R_{exp}	1.6	1.8	1.7	1.6
R_{wp}	3.1	2.2	1.9	4.2
$GooF$	1.9	1.3	1.2	2.6
Phase fraction	99 %	96 %	99 %	11 %
Side phase(s)	1 % La_2SeO_2	4 % Ce_2SeO_2	1 % Pr_2SeO_2	64 % $NdCrSe_2O$ 25 % Nd_2SeO_2

The unit cell parameters a , b and c decrease with the effective radii of the rare-earth metal ions while the monoclinic angle β varies only slightly and shows a maximum for Ce (Fig. S5). As a consequence, the cell volume also decreases with smaller effective rare-earth radii. Comparing the compounds $mC\text{-La}_2T\text{Se}_2\text{O}_2$ ($T = \text{Cr, Fe, Mn}$) in Figure 3, the cell volume of $\text{La}_2\text{CrSe}_2\text{O}_2$ is in between these of $mC\text{-La}_2\text{MnSe}_2\text{O}_2$ and $mC\text{-La}_2\text{FeSe}_2\text{O}_2$, which is consistent with the trend of the ionic radii of the transition metal. Furthermore, it is noticeable that in case of the manganese and iron compounds, it is not possible to prepare compounds with smaller rare-earth metals as lanthanum or cerium, respectively, whereas $\text{Pr}_2\text{CrSe}_2\text{O}_2$ and $\text{Nd}_2\text{CrSe}_2\text{O}_2$ are accessible via the synthesis route described here. In contrast to the manganese and iron compounds, we found no other polymorphs of $\text{RE}_2\text{CrSe}_2\text{O}_2$ by scanning different reaction temperatures from 1073–1373 K.

Figure 3. Unit cell volumes versus the effective radii²¹ of the respective rare-earth metal of $mC\text{-La}_2\text{MnSe}_2\text{O}_2$, $mC\text{-RE}_2\text{FeSe}_2\text{O}_2$ ($\text{RE} = \text{La, Ce}$) and $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{La-Nd}$). Data points of the iron compounds are taken from the literature.⁵

Low Temperature Structural Phase Transition

X-ray and neutron powder diffraction patterns of $\text{La}_2\text{CrSe}_2\text{O}_2$ reveal peak splitting below ≈ 200 K, exemplarily shown on the (111) reflection in Figure 4a. Generally, the reflections of the monoclinic phase $(hkl)_m$ gradually split into two reflection types that can be indexed as $(hkl)_t$ and $(h-k)_t$ reflections of a triclinic phase. Rietveld refinement using space group $P\bar{1}$ is shown exemplarily for $T = 20$ K in Figure S3 and gives excellent fit to the experimental data. Subsequent low temperature X-ray and neutron diffraction experiments between 300 and 4 K revealed continuously decreasing cell parameters a , b , c and shrinking unit cell volumes by 0.95 %, 0.23 %, 0.21 % and 0.51 %, respectively (Fig. S9). The distortion of the unit cell, which affects primarily the unit cell angle α , is obvious below $T_{tr} = 200$ K, as depicted in Figure 4b. While the unit cell angles β and γ decrease slightly upon cooling (0.03 % and 0.15 %), there is a significant change of 1.00 % for α , which finally requires the symmetry reduction to $P\bar{1}$. The transition is reversible and non hysteretic upon heating the sample to room temperature again.

Figure 4. a) Peak splitting of the (111) reflection of the monoclinic phase of $\text{La}_2\text{CrSe}_2\text{O}_2$ into (111) and $(\bar{1}\bar{1}1)$ reflections of the triclinic phase at different temperatures. b) Evolution of the unit cell angles α and γ upon cooling including data from powder X-ray and neutron diffraction experiments. Error bars are smaller than the data points.

The Cr-O bond lengths in the CrSe_4O_2 -octahedra of $\text{La}_2\text{CrSe}_2\text{O}_2$ remain almost constant upon cooling, whereas the Cr-Se bond lengths split from 4 x 281.9(1) pm into two shorter (272.4(1) or 274.5(1) pm) and two longer (288.1(1) or 291.3(1) pm) ones for Cr1 and Cr2, respectively. This distortion of the CrSe_4 -plane from square to rhombic is depicted in Figure 5. All Se-Cr-Se bond angles remain within $90 \pm 0.5^\circ$ while the O-Cr-Se bond angles deform from $89.2(1)$ – $90.8(1)^\circ$ to $87.6(1)$ – $92.4(1)^\circ$ at low temperatures. The d^4 high-spin configuration of Cr^{2+} is a typical Jahn-Teller case which drives a distortion stabilizing the x^2-y^2 or z^2 orbital. In the $C2/m$ phase the occupied x^2-y^2 is already below the empty z^2 because of the closer apical oxygen ligands. Nevertheless the rhombic distortion of the square of selenium atoms reduces the overlap of the x^2-y^2 orbital and further reduces its energy ($\Delta E_2 > \Delta E_1$ in Fig. 5). Since we do not come from a degenerate state in the $C2/m$ phase, we refer this to a second order Jahn-Teller distortion.

Figure 5. Selected bond lengths in the CrSe_4O_2 -octahedra obtained from Rietveld fits of neutron diffraction data at 300 K (left) and 4 K (right). Schematic crystal field splittings (middle) for an undistorted octahedral as well as for compressed octahedral (at 300 and 4 K) geometries of the $\text{Cr}^{2+}\text{Se}_4\text{O}_2$ polyhedron.

We observed this effect in $\text{Ce}_2\text{CrSe}_2\text{O}_2$ at a significantly lower transition temperature of $T_{\text{tr}} = 130$ K (Fig. S10). The trend of the unit cell parameters of $\text{Ce}_2\text{CrSe}_2\text{O}_2$ upon cooling is depicted in Figure S11. In contrast, $\text{Pr}_2\text{CrSe}_2\text{O}_2$ does not show any phase transition down to 10 K

(Fig. S12, S13). Similar observations were made by *Tuxworth et al.* for $RE_4TiSe_4O_4$ ($RE = \text{Sm–Er, Y}$) compounds. The materials with the largest rare-earth ions, $\text{Sm}_4\text{TiSe}_4\text{O}_4$ and $\text{Gd}_4\text{TiSe}_4\text{O}_4$, show a phase transition at low temperatures which could be an order-disorder transition of the displaced titanium atoms in the distorted TiSe_4O_2 -octahedra.²⁰

Magnetic Properties

Magnetic measurements of $RE_2\text{CrSe}_2\text{O}_2$ ($RE = \text{La–Pr}$) reveal Curie-Weiss behavior down to ~ 20 K (Fig. 6) with effective moments of 5.01(1) [4.90], 6.06(3) [6.08] and 7.24(1) [7.05] μ_B per formula unit for $RE = \text{La, Ce and Pr}$, respectively (theoretical values in square brackets). The theoretical effective moments are calculated by taking the square root of the sum of the squares of the theoretical moments (μ_{th}) of the contributing magnetic cations, i.e. $\mu_{\text{eff}}(RE_2\text{CrSe}_2\text{O}_2) = [2\mu_{\text{th}}(RE^{3+})^2 + \mu_{\text{th}}(\text{Cr}^{2+})^2]^{1/2}$, with $\mu_{\text{th}}(\text{Ce}^{3+}) = 2.53 \mu_B$, $\mu_{\text{th}}(\text{Pr}^{3+}) = 3.58 \mu_B$ and $\mu_{\text{th}}(\text{Cr}^{2+}) = 4.90 \mu_B$. Abruptly decreasing susceptibilities below 14–17 K indicate antiferromagnetic ordering similar to $mC\text{-La}_2\text{FeSe}_2\text{O}_2$ ($T_N = 20$ K) and $mC\text{-La}_2\text{MnSe}_2\text{O}_2$ ($T_N = 15$ K).⁵

Figure 6. Magnetic susceptibilities (black) and inverse susceptibilities (inset) of $\text{La}_2\text{CrSe}_2\text{O}_2$ (top), $\text{Ce}_2\text{CrSe}_2\text{O}_2$ (middle) and $\text{Pr}_2\text{CrSe}_2\text{O}_2$ (bottom). $B = 1$ T. Curie-Weiss fits in red. Parameters obtained from the fits are given in the inset. Measurements were performed on free and randomly oriented powders.

Isothermal magnetizations of $\text{La}_2\text{CrSe}_2\text{O}_2$ and $\text{Ce}_2\text{CrSe}_2\text{O}_2$ at 300 and 1.8 K are linear as expected (Fig. S6–7). $\text{Pr}_2\text{CrSe}_2\text{O}_2$ shows a remarkable upturn of the magnetization at higher

fields > 5 T at 3 K (Fig. 7) and > 3 T at 1.8 K (Fig. S8). Figure 7 displays the magnetization isotherms of $\text{Pr}_2\text{CrSe}_2\text{O}_2$ measured at 3, 10, 20, and 50 K. The isotherms measured at 3 (red) and 10 K (blue), both below the Néel temperature, display a slight curvature at a critical field of $H_{\text{Cr}} \sim 50$ kOe. This indicates an antiferromagnetic-to-ferromagnetic spin-reorientation, also referred to as metamagnetic transition. Furthermore the 3 K isotherm exhibits a weak but well resolved hysteresis between 50 and 90 kOe in the increasing / decreasing field curves. Such features are rarely observed, one example is $\text{Pr}_2\text{Pd}_2\text{Mg}$ ²². Magnetic moments of $1.77(1) \mu_{\text{B}}$ per formula unit at 3 and 10 K and 90 kOe were found; substantially reduced when compared with the theoretical saturation moment of $3.20 \mu_{\text{B}}$ per praseodymium atom. We assume that the Cr^{2+} contribution is small as found in $\text{La}_2\text{CrSe}_2\text{O}$. The isotherms at 20 and 50 K show the typical linear temperature dependence of the magnetization as expected for a paramagnetic material (above the Néel temperature).

Figure 7. Magnetization isotherms of $\text{Pr}_2\text{CrSe}_2\text{O}_2$ at 3, 10, 20, and 50 K. The isotherms at 3 and 10 K, below the ordering temperature, exhibit a spin reorientation at $H_{\text{Cr}} \sim 50$ kOe, in addition the 3 K isotherm shows a hysteresis (enlarged in the inset) between 50 and 90 kOe.

Muon Spin Rotation and Relaxation

Zero field (ZF) and weak transverse field (wTF) muon spin rotation and relaxation (μ SR)²³ measurements have been performed on a powder sample of $\text{La}_2\text{CrSe}_2\text{O}_2$ to obtain further insight into the magnetic ordering of this compound. In Figure 8a, representative ZF- μ SR spectra are shown for various temperatures. Above T_N , the muon spin polarization $P(t)$ is only weakly exponentially damped which is typical for a paramagnetic specimen with fast fluctuating electronic spins and randomly oriented and partly diluted nuclear moments. Below T_N , spontaneous muon spin precession is observed indicating the development of static internal magnetic fields B_i at the interstitial muon stopping sites within the lattice. The Fourier transform of the data which is depicted in Figure 8b reveals the presence of two distinct precession frequencies $f_i = \frac{\gamma}{2\pi} B_i$ due to two magnetically inequivalent muon sites (with the gyromagnetic ratio of the muon $\gamma = 2\pi \cdot 135.5 \text{ MHz/T}$). Such well-defined fields at the muon sites prove the long range commensurate character of the magnetic ordering, because incommensurate magnetic order would lead to a broad distribution of internal fields.

Figure 8. a) Representative ZF- μ SR spectra of $\text{La}_2\text{CrSe}_2\text{O}_2$ showing muon spin precession due to the presence of static internal magnetic fields below T_N . Offset of the data is +0.25 (blue) and +0.5 (red and orange), respectively. b) The Fourier transform of the raw data reveals that several magnetic inequivalent muon sites exist within the magnetic structure and that the magnetic structure is commensurate with the lattice.

Details of the fit of the μ SR data is given in the supplementary information. In Figure 9 the extracted fit parameters are depicted. A gradual decrease of the frequencies $f_i(T)$, i.e. internal magnetic fields, is observed towards the Néel temperature of about 13 K. Additionally, a peak is observed in the spin-lattice relaxation rate λ_L at T_N . Both these features are characteristic for a second order magnetic phase transition. Results of the wTF- μ SR measurements which are able to determine the non-magnetic volume fraction of the sample are shown in Figure 9d. From these results it is obvious that through a sharp transition essentially the full sample volume orders magnetically at $T_N^{50\%} = 12.7(3)$ K. An unusual feature of our measurements is reported in

Figure 9c. The ratio f_1/f_2 of the two frequencies changes dramatically as a function of temperature. In a rigid magnetic structure where only the magnetic order parameter increases as a function of decreasing temperature such a ratio is expected to be constant and both frequencies are an equivalent measure of the size of the ordered magnetic moment. The fact that f_1/f_2 is not constant as a function of temperature could therefore originate from a continuous change of the magnetic structure on lowering the temperature e.g. in the form of a changing canting angle of the antiferromagnetic structure. Since μ SR is a local probe technique, this conclusion is only rather indirect and awaits further experimental verification e.g. by temperature dependent neutron scattering experiments well below the Néel temperatures.

Figure 9. Results of the analysis of μ SR measurements on $\text{La}_2\text{CrSe}_2\text{O}_2$. Temperature dependence of the spontaneous precession frequencies (a) and the longitudinal relaxation rate λ_L (b) from ZF- μ SR. c) Ratio of the frequencies. d) Temperature dependence of the non-magnetic

volume fraction determined by wTF- μ SR showing a sharp transition of essentially the full sample volume at $T_N = 12.7(3)$ K.

Neutron Diffraction - Low Temperature Magnetic Structure of $\text{La}_2\text{CrSe}_2\text{O}_2$

Powder neutron diffraction experiments at low temperature were performed in order to characterize the magnetic ordering of $\text{La}_2\text{CrSe}_2\text{O}_2$ exemplarily for the $mC\text{-}RE_2T\text{Se}_2\text{O}_2$ compounds ($RE = \text{La-Nd}$; $T = \text{Cr-Fe}$) with similar magnetic susceptibility curves. The neutron powder diffraction pattern at 4 K, well below T_N , is plotted in Figure 10. Several strong magnetic reflections appear at $\approx 12.9, 15.2, 16.2, 21.9, 22.9$ and $24.7^\circ 2\theta$ (labelled as m1–m6). The magnetic structure cannot be described within the crystallographic unit cell but requires a commensurate propagation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which means doubling of the nuclear unit cell in all three dimensions. Refinements of the magnetic structure were performed in space group $P\bar{1}$ using the program FullProf¹⁸. Assuming antiferromagnetic ordering with magnetic moments of Cr(1) and Cr(2) constrained to have the same magnitude gives excellent fits to the experimental data as can be seen in the Rietveld profile in Figure 10. Detailed information of the refinements (CIF files) is given in the supporting information.

Figure 10. Neutron powder diffraction pattern of $\text{La}_2\text{CrSe}_2\text{O}_2$ (blue) with Rietveld fit (red) and difference plot (gray) at 4 K. Inset: Magnification of the pattern between $11^\circ \leq 2\theta \leq 25.5^\circ$. Peaks marked with m_i ($i = 1-6$) are magnetic Bragg reflections.

The magnetic cell has the dimensions $\approx 23.0 \text{ \AA} \times 7.9 \text{ \AA} \times 14.3 \text{ \AA}$. Figure 11 shows the magnetic structure of $\text{La}_2\text{CrSe}_2\text{O}_2$ with absolute values of the magnetization vectors along the non-orthogonal unit cell axes $(M_a, M_b, M_c) = (1.07(14) \mu_B, 1.46(11) \mu_B, 3.47(8) \mu_B)$ and an ordered magnetic moment of $3.40(4) \mu_B$ per Cr^{2+} atom at 4 K. The spin arrangement is G-type antiferromagnetic. Crystallographic data of $\text{La}_2\text{CrSe}_2\text{O}_2$ at 4 and 20 K can be found in Table S2.

Figure 11. Magnetic ordering pattern of Cr^{2+} (green) in $\text{La}_2\text{CrSe}_2\text{O}_2$ at 4 K. The magnetic cell is doubled in all three directions in comparison to the nuclear cell (propagation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$). Cr1 is dark green and Cr2 lime.

CONCLUSION

Crystals of the new members of $\text{RE}_2\text{CrSe}_2\text{O}_2$ ($\text{RE} = \text{La-Nd}$) compounds were grown in a NaI/KI flux. Single crystal X-ray diffraction identified the $\text{Pb}_2\text{HgCl}_2\text{O}_2$ structure type in space group $C2/m$. $\text{La}_2\text{CrSe}_2\text{O}_2$ and $\text{Ce}_2\text{CrSe}_2\text{O}_2$ undergo structural phase transitions to triclinic $P\bar{1}$ symmetry at ≈ 200 and 130 K, respectively, which are probably driven by the second order Jahn-Teller effect of the Cr^{2+} ions. Magnetometry revealed Curie-Weiss paramagnetism and indicated antiferromagnetic order below $T_N \approx 14\text{--}17$ K. $\text{Pr}_2\text{CrSe}_2\text{O}_2$ shows an antiferromagnetic-to-ferromagnetic spin reorientation (metamagnetism) at higher magnetic fields. Muon spin rotation experiments with $\text{La}_2\text{CrSe}_2\text{O}_2$ confirm a second order transition into a commensurate magnetic structure, which is proved by 4 K neutron powder diffraction data. The magnetic structure is G-type antiferromagnetic with an ordered Cr^{2+} moment of $3.40(4) \mu_B$ at 4 K.

ASSOCIATED CONTENT

Supporting Information

Powder X-ray diffraction patterns including Rietveld fits, isothermal magnetization measurements, plots of the lattice parameters (on cooling), crystallographic data of $\text{La}_2\text{CrSe}_2\text{O}_2$ from single crystal X-ray and powder neutron diffraction data, details of muon spin rotation and relaxation measurements. This material is available as PDF file. Crystallographic and magnetic data of $\text{La}_2\text{CrSe}_2\text{O}_2$ in CIF format is available free of charge via the Internet at <http://pubs.acs.org>. Information on the structure determination of $\text{La}_2\text{CrSe}_2\text{O}_2$ can be obtained free of charge at Fachinformationszentrum Karlsruhe, 76355 Eggenstein-Leopoldshafen, Germany [fax (+49)7247-808-666; email: crysdata@fiz-karlsruhe.de, web site http://www.fiz-karlsruhe.de/request_for_deposited_data.html) upon quoting the CSD number 432290.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Crystals of the new paramagnetic oxyselenides $RE_2CrSe_2O_2$ were grown in salt fluxes. The monoclinic crystal structures with *high-spin- d^4* Cr^{2+} undergo second order Jahn-Teller distortions and exhibit three-dimensional ordering of the magnetic moments (G-type) below $T_N = 14\text{--}17$ K according to neutron diffraction and muon spin rotation experiments.

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