

## Article

# Single Crystal Growth and Physical Properties of Pyroxene $\text{CoGeO}_3$

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**Abstract:** We report on the synthesis and physical properties of cm-sized  $\text{CoGeO}_3$  single crystals grown in a high pressure mirror furnace at pressures of 80 bar. Direction dependent magnetic susceptibility measurements on our single crystals reveal highly anisotropic magnetic properties that we attribute to the impact of strong single ion anisotropy appearing in this system with  $T_N \sim 33.5$  K. Furthermore, we observe effective magnetic moments that are exceeding the spin only values of the Co ions, which reveals the presence of sizable orbital moments in  $\text{CoGeO}_3$ .

**Keywords:** floating zone method; single crystal growth; pyroxene; magnetic susceptibility; X-ray diffraction; X-ray absorption spectroscopy



**Citation:** Zhao, L.; Hu, Z.; Guo, H.; Geibel, C.; Lin, H.-J.; Chen, C.-T.; Khomskii, D.; Tjeng, L.H.; Komarek, A.C. Single Crystal Growth and Physical Properties of Pyroxene  $\text{CoGeO}_3$ . *Crystals* **2021**, *11*, 378. <https://doi.org/10.3390/cryst11040378>

Academic Editor: Yuui Yokota

Received: 16 March 2021

Accepted: 1 April 2021

Published: 5 April 2021

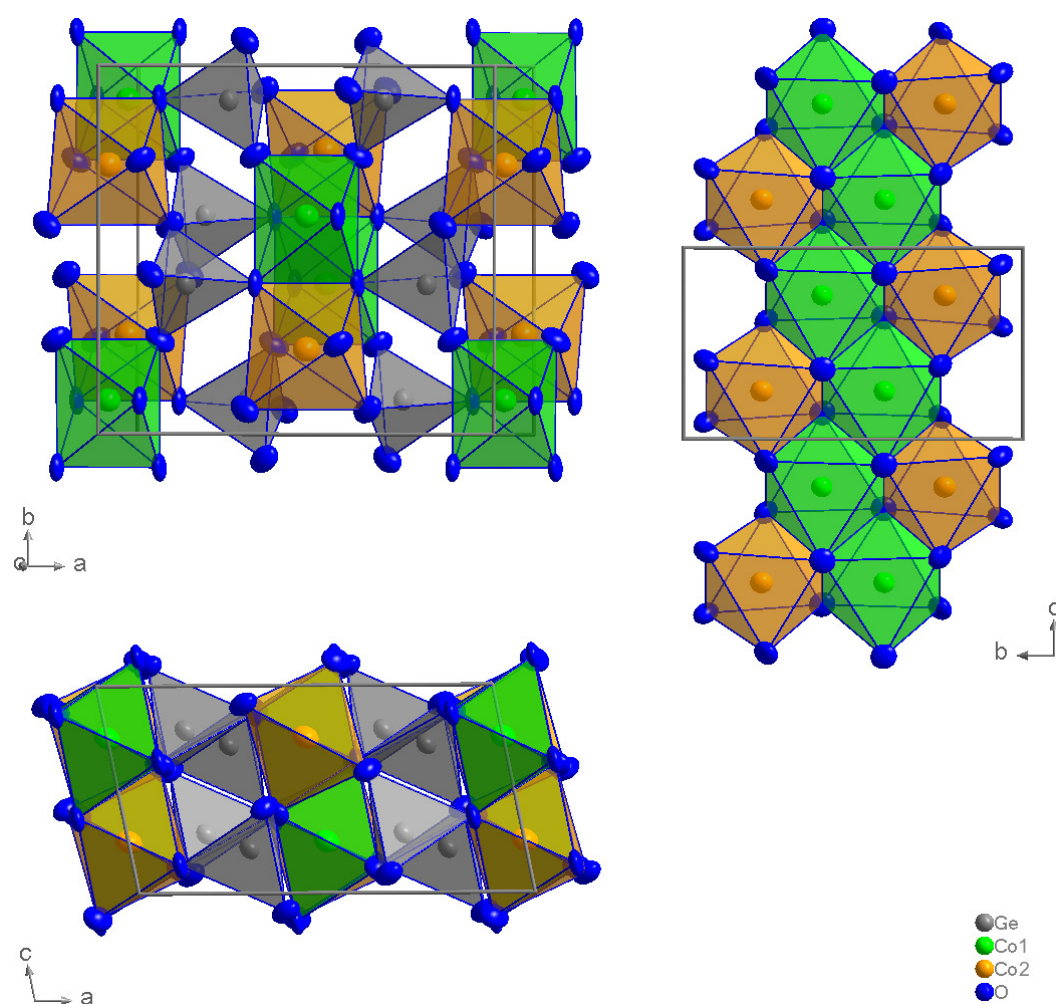
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## 1. Introduction

Pyroxenes are one of the main rockforming minerals in the Earth's crust [1–4] and have the general formula  $AMX_2O_6$  ( $A$  = mono- or divalent metal,  $M$  = di- or trivalent metal,  $X = \text{Si}^{4+}$ ,  $\text{Ge}^{4+}$  or  $\text{V}^{5+}$ ). This class of materials gained considerable interest due to their large amount of diverse properties [5,6] including the observation of multiferroicity and magnetoelectric effects [7]. The quasi 1D system  $\text{CoGeO}_3$  having two Co sites belongs to the family of pyroxene minerals [8] and crystallizes in two polymorphs [8,9]—the monoclinic polymorph is stable above 1351 °C and the orthorhombic one below this temperature [9]. As reported in literature, single crystals of the monoclinic phase with space group  $C2/c$  ( $a = 9.64$  Å,  $b = 8.99$  Å,  $c = 5.15$  Å and  $\beta = 101^\circ 10'$ ) have been grown from the melt with crystal sizes of the order of  $1 \times 0.25 \times 0.1$  mm<sup>3</sup> [9]. The corresponding pyroxene structure of monoclinic  $\text{CoGeO}_3$  [10] consist of Co1 ions that are forming  $\text{CoO}_6$  octahedral zigzag chains running in  $c$ -direction, with adjacent Co2 octahedra, compare Figure 1. The so formed Co ladders (or double-zig-zag chains) are separated by  $\text{GeO}_4$  tetrahedra from each other. Throughout this article, we refer to the monoclinic form of  $\text{CoGeO}_3$ , which orders antiferromagnetically below  $T_N \sim 36$  K [8].



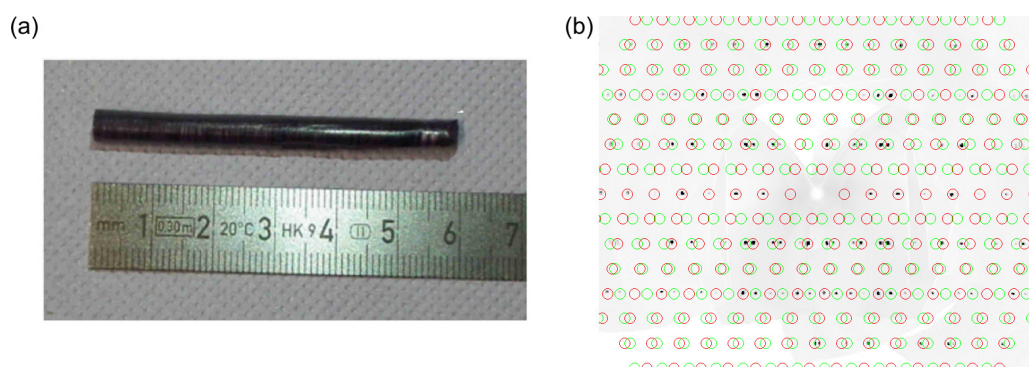
**Figure 1.** Crystal structure of  $\text{CoGeO}_3$ . The atoms are indicated by 99.9% probability ellipsoids obtained from single crystal X-ray diffraction (see Tables 1 and 2); grey: germanium (Ge1), green: cobalt (Co1), dark yellow: cobalt (Co2) and blue: oxygen (O1–O3) atoms.

## 2. Results and Discussion

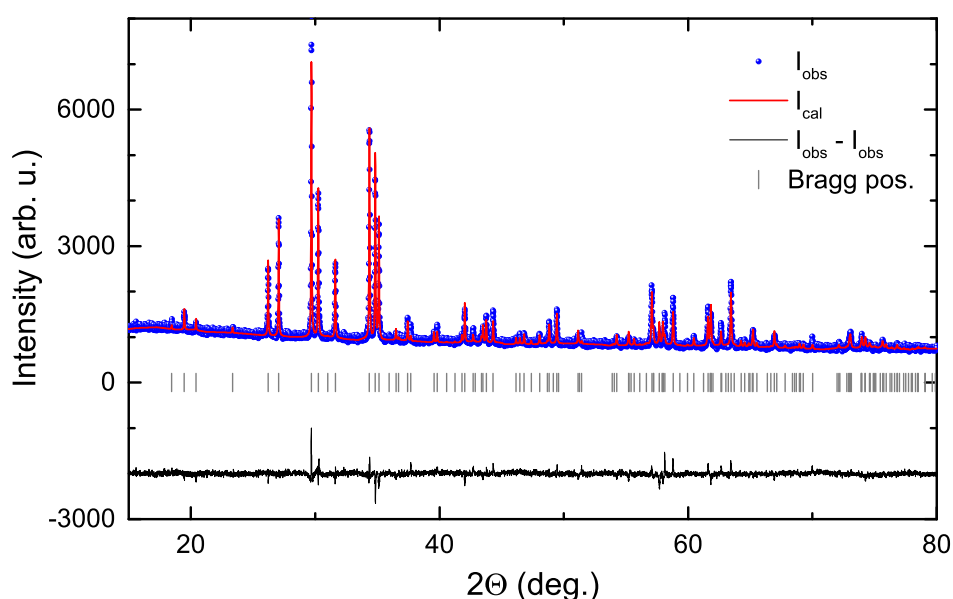
A photo of our several  $\text{cm}^3$ -sized, as-grown single crystal of  $\text{CoGeO}_3$  is shown in Figure 2a. Powder XRD measurements performed on crushed and powderized parts of the single crystal indicate an impurity-free monoclinic phase, compare Figure 3. The lattice parameters obtained from a Rietveld-refinement can be found in the crystal structure table (Table 1). X-ray Laue and single crystal X-ray diffraction measurements indicate the single crystalline nature of our as-grown crystal. As can be seen in Figure 2b, the single crystals are twinned with the underlying twin matrix  $(-1\ 0\ -0.732, 0\ 1\ 0, 0\ 0\ 1)$ . A precise structural analysis by means of single crystal X-ray diffraction has been performed which confirms that we have synthesized the monoclinic pyroxene  $\text{CoGeO}_3$ —see Tables 1 and 2. The resulting positional parameters ( $x, y, z$ ) for the six different atoms in the asymmetric unit are in agreement with literature data [10], but within the high precision of our measurement we were additionally able to determine the anisotropic displacement parameters—see Tables 1 and 2. From the obtained structural parameters, the accurate bond distances could also be determined, see Table 3. According to the bond valence sum (BVS) formalism, these results indicate Co oxidation states that are very close to  $2+$ , see Table 3.

The oxidation state of the Co ions in  $\text{CoGeO}_3$  was further investigated by soft X-ray absorption spectroscopy (XAS) measurements at the Co  $L_{2,3}$  edge in the total electron yield mode using a CoO single crystal as a  $\text{Co}^{2+}$  reference. The similarity of the Co- $L_{2,3}$  XAS spectra of  $\text{CoGeO}_3$  and CoO, see Figure 4, reveals a  $\text{Co}^{2+}$  high spin state in octahedral

coordination [11–13] in  $\text{CoGeO}_3$ . These observations corroborate the results of the BVS for the Co ions and further confirm the stoichiometry of our single crystals.



**Figure 2.** (a) Single crystal of  $\text{CoGeO}_3$  grown in a high pressure mirror furnace; (b) intensities in the  $H0L$  plane of reciprocal space measured by means of single crystal X-ray diffraction, compare Table 1. These measurements reveal twinning in our single crystals with the twin law matrix  $(-1\ 0\ -0.732, 0\ 1\ 0, 0\ 0\ 1)$ . The green and red circles indicate reflections belonging to twin domain A or B.



**Figure 3.** Powder X-ray diffraction pattern of a crushed  $\text{CoGeO}_3$  single crystal.

The magnetic susceptibility  $\chi$  of  $\text{CoGeO}_3$  shows a drop at  $T_N \sim 33.5$  K, see Figure 5. The transition to an antiferromagnetic state is in agreement with literature [8]. The availability of sizeable single crystals allowed us to measure also the direction dependence of the magnetic susceptibility. These direction dependent measurements (with  $H \parallel c$  and  $H \perp c$ ) reveal a highly anisotropic behavior of  $\chi$ . The Weiss temperatures  $\Theta_W$  obtained from Curie–Weiss fits even have different signs for  $H \parallel c$  and  $H \perp c$  and amount to 45.08 K and  $-49.55$  K, respectively. This strong anisotropy arises from the presence of single ion anisotropy in the system which is typical for  $\text{Co}^{2+}$ -ions [11,14]. Moreover, the corresponding effective moments  $\mu_{\text{eff}}$  amount to  $4.76 \mu_B$  and  $5.18 \mu_B$  respectively. The value of the effective moments in  $\text{CoGeO}_3$  is much larger than the theoretical spin-only value for  $\text{Co}^{2+}$  ions of  $3.87 \mu_B$  and suggests that the  $\text{Co}^{2+}$  ions are in a high spin state with large orbital moment contributions. For powder samples, the Weiss temperatures  $\Theta_W$  amount to 6.46 K with effective moments  $\mu_{\text{eff}}$  of  $4.98 \mu_B$ .

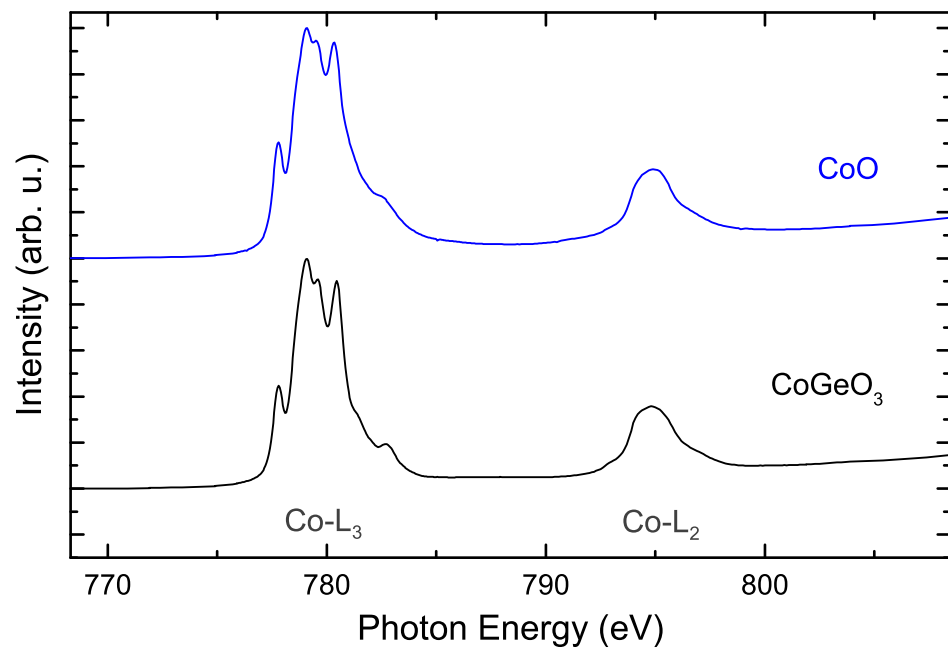


Figure 4. (Isotropic) X-ray absorption spectra of CoGeO<sub>3</sub> and of CoO at the Co L<sub>2,3</sub> edge.

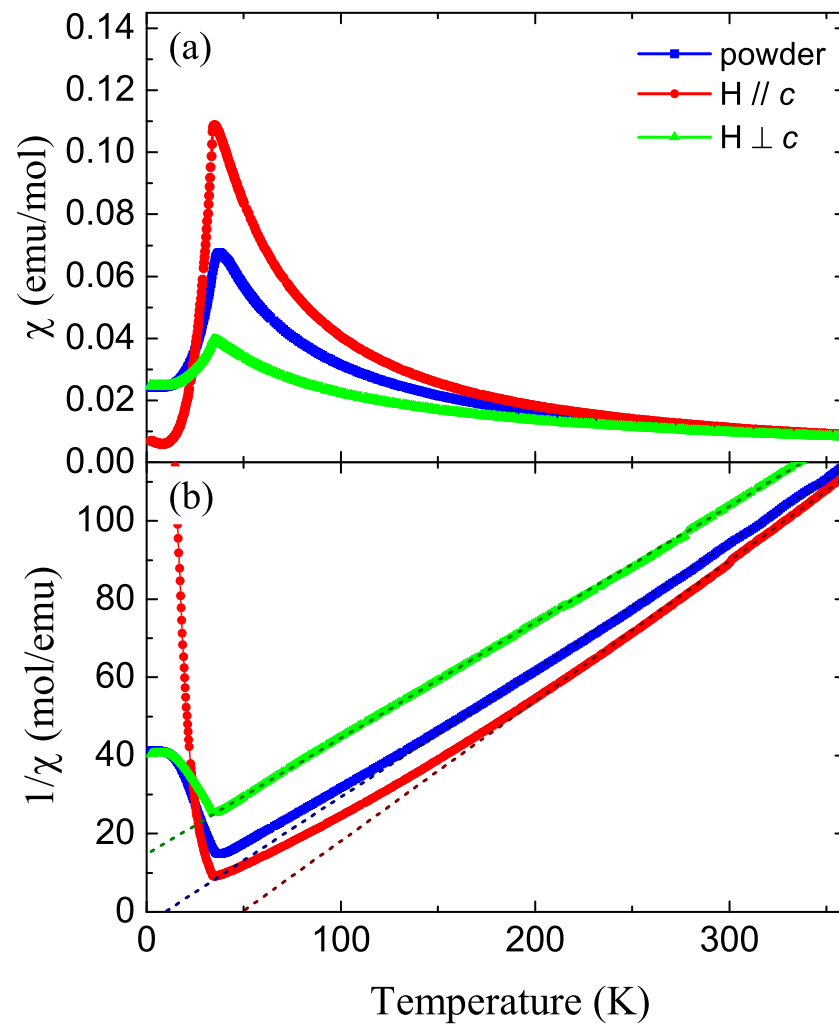


Figure 5. (a) Direction dependent magnetic susceptibility ( $\chi$ ) of CoGeO<sub>3</sub> single crystals measured in a field of  $\mu_0 H = 0.1$  T. For comparison also the values for a CoGeO<sub>3</sub> powder sample are shown. (b) The inverse of the magnetic susceptibility ( $\chi^{-1}$ ).

**Table 1.** Crystallographic and structural refinement data of a single crystal X-ray diffraction measurement. The crystallographic software *Jana* was used for the structural refinement [15]. The lattice parameters were obtained from a powder X-ray diffraction measurement using Cu K $\alpha$ 1 radiation (Rietveld refinement with *Fullprof* [16];  $\chi^2 = 2.24$ ). [\* : unobserved reflections were also used.]

Empirical formula	CoGeO <sub>3</sub>
Formula weight (g/mol)	179.5
Temperature	room temperature
Wavelength	Mo K $\alpha$
Crystal system	monoclinic
Space group	<i>C</i> 2/c (15)
Unit cell dimensions	$a = 9.6623(2) \text{ \AA}$ $b = 8.9928(2) \text{ \AA}$ $c = 5.16980(10) \text{ \AA}$ $\beta = 101.2785(10)^\circ$
Volume	440.535(16) $\text{\AA}^3$
Z	8
Density (g/cm <sup>3</sup> )	5.4134
Absorption coefficient $\mu$	20.861
<i>F</i> (000)	664
Crystal size	~10–20 $\mu\text{m}$
$2\Theta_{\text{max}}$	106.58°
Index range	$h$ : −21 → 21 $k$ : −19 → 20 $l$ : −11 → 10
Reflections in total / independent	13,219/2438
Observed reflections / independent	10,541/2078
Internal R-value	2.31%
Completeness up to $2\Theta_{\text{max}}$	91.48%
Absorption correction	multi-scan
Min. / max. transmission	0.3738 / 0.7505
Refinement method	least squares on $F^2$
Reflections threshold *	$I > 5\sigma(I)$
Goodness of fit	1.97
R / $R_w$	1.63 / 5.28%
Largest minima in Fourier difference	−3.10 e <sup>−</sup> $\text{\AA}^{-3}$
Largest maxima in Fourier difference	2.78 e <sup>−</sup> $\text{\AA}^{-3}$

**Table 2.** Refinement results of single crystal X-ray diffraction measurements of CoGeO<sub>3</sub>. Our structural results are in fair agreement with older data in literature that contain only isotropic temperature factors *B* [10].

Atom	x	y	z
Ge1	0.30104(2)	0.09381(2)	0.21471(4)
Co1	0	0.09179(4)	0.75
Co2	0	0.26966(4)	0.25
O1	0.11779(15)	0.09052(14)	0.1358(3)
O2	0.38225(14)	0.24390(16)	0.3830(3)
O3	0.36047(15)	0.06723(16)	0.9099(3)

Table 2. Cont.

atom	$U_{11}$ ( $\text{\AA}^2$ )	$U_{22}$ ( $\text{\AA}^2$ )	$U_{33}$ ( $\text{\AA}^2$ )
Ge1	0.00347(12)	0.00445(13)	0.00401(12)
Co1	0.00526(17)	0.00499(19)	0.00458(18)
Co2	0.00622(16)	0.00571(17)	0.00483(16)
O1	0.0020(5)	0.0075(6)	0.0067(5)
O2	0.0074(5)	0.0062(5)	0.0059(5)
O3	0.0077(6)	0.0071(5)	0.0052(5)
atom	$U_{12}$ ( $\text{\AA}^2$ )	$U_{13}$ ( $\text{\AA}^2$ )	$U_{23}$ ( $\text{\AA}^2$ )
Ge1	−0.00022(5)	0.00010(8)	−0.00009(5)
Co1	0	0.00021(13)	0
Co2	0	0.00010(12)	0
O1	0.0003(4)	0.0003(5)	−0.0003(4)
O2	−0.0025(4)	−0.0001(4)	−0.0012(4)
O3	−0.0019(5)	0.0027(5)	−0.0014(4)

Table 3. Bond lengths and bond valence sums (BVS) in  $\text{CoGeO}_3$ . BVS parameters were taken from Ref. [17].

Atoms	Distance ( $\text{\AA}$ ) / BVS
Ge1-O1	1.7399(14)
Ge1-O2	1.7142(14)
Ge1-O3	1.7965(18)
Ge1-O3	1.7963(15)
<b>BVS(Ge1)</b>	<b>3.896(8)</b>
Co1-O1	2.0959(15)
Co1-O1	2.0959(15)
Co1-O1	2.1458(15)
Co1-O1	2.1458(15)
Co1-O2	2.0649(16)
Co1-O2	2.0649(16)
<b>BVS(Co1)</b>	<b>1.999(3)</b>
Co2-O1	2.1229(15)
Co2-O1	2.1229(15)
Co2-O2	2.0157(15)
Co2-O2	2.0157(15)
Co2-O3	2.2588(17)
Co2-O3	2.2588(17)
<b>BVS(Co2)</b>	<b>1.894(3)</b>

### 3. Materials and Methods

The floating zone growth of monoclinic  $\text{CoGeO}_3$  was carried out in a high pressure optical mirror furnace (HKZ, *SciDre GmbH*). Initially,  $\text{Co}_3\text{O}_4$  and  $\text{GeO}_2$  with an excess of 3%  $\text{GeO}_2$  were mixed together and sintered at 1200 °C for 72 h with intermediate grindings. From these powders, polycrystalline rods were made using a hydrostatic press and subsequently sintered at 1300 °C for 24 h.

During the floating zone growth, pressures of 80 bar of an Argon/ $\text{O}_2$  mixture (with a ratio of 98:2) were used and a growth rate of 3.6 mm per hour was successful for growing large (twined)  $\text{CoGeO}_3$  single crystals (heating power  $\sim 2700$  W).

Powder and single crystal X-ray diffraction (XRD) measurements have been performed on a Bruker D8 Discover A25 (Cu  $K_{\alpha 1}$  radiation) and on a Bruker D8 VENTURE diffractometer (Mo  $K_{\alpha}$  radiation), respectively.



Soft X-ray absorption spectroscopy measurements have been performed at the BL11A Beamline of National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. The Co- $L_{2,3}$  edge were recorded in the total electron yield method with a probing depth of about 40 Å [18]. The samples were cleaved in-situ under ultra-high vacuum conditions to ensure atomically clean sample surfaces. The pressure in the measurement chamber is in the low  $10^{-10}$  mbar range.

Direction dependent magnetic properties of single crystals of  $\text{CoGeO}_3$  were initially studied using a SQUID magnetometer (MPMS-5XL, Quantum Design Inc.).

#### 4. Conclusions

We have grown sizable single crystals of  $\text{CoGeO}_3$  in a high pressure floating zone furnace that were characterized by XRD and XAS measurements. Our direction dependent magnetic susceptibility measurements on our single crystals reveal highly anisotropic magnetic properties with large effective moments of  $\sim 5 \mu_B$  per Co ion, which are indicative for (i) the significance of single ion anisotropy and (ii) the occurrence of large orbital moments in this system.

**Author Contributions:** Floating zone growth: A.C.K. and L.Z.; Magnetic susceptibility measurements: L.Z.; powder and single crystal XRD measurements: A.C.K. measurements: L.Z., Z.H. and H.-J.L.; Interpretation and writing: L.Z., Z.H., H.G., C.G., H.-J.L., C.-T.C., D.K., L.H.T. and A.C.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** The research in Dresden was partially funded by the Deutsche Forschungs-gemeinschaft through SFB 1143 (Project-Id 247310070) and the work in Cologne (D. I.K.) by the Deutsche Forschungs-gemeinschaft through CRC 1238 (Project-Id 277146847).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author upon request.

**Acknowledgments:** We acknowledge support for the XAS experiments from the Max Planck-POSTECH-Hsinchu Center for Complex Phase Materials.

**Conflicts of Interest:** The authors declare no conflict of interest.

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