Article

Single Crystal Growth and Physical Properties of Pyroxene CoGeO$_3$

Li Zhao $^1$, Zhiwei Hu $^1$, Hanjie Guo $^{1,2,}$, Christoph Geibel $^1$, Hong-Ji Lin $^3$, Chien-Te Chen $^3$, Daniel Khomskii $^4$, Liu Hao Tjeng $^1$ and Alexander C. Komarek $^1,*$

1 Max-Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, D-01187 Dresden, Germany; lzhao1027@outlook.com (L.Z.); Zhiwei.Hu@cpfs.mpg.de (Z.H.); hjguo@sslab.org.cn (H.G.); Christoph.Geibel@cpfs.mpg.de (C.G.); Hao.Tjeng@cpfs.mpg.de (L.H.T.)
2 Neutron Science Platform, Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China
3 National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30076, Taiwan; hjlin@nsrrc.org.tw (H.-J.L.); ctchen@nsrrc.org.tw (C.-T.C.)
4 Physics Institute II, University of Cologne, Zülpicher Str. 77, 50937 Cologne, Germany; khomskii@ph2.uni-koeln.de
* Correspondence: Alexander.Komarek@cpfs.mpg.de; Tel.: +49-351-4646-4423

Abstract: We report on the synthesis and physical properties of cm-sized 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 CoGeO$_3$.

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

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, $X$ = Si$^{4+}$, Ge$^{4+}$ or 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 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 $\beta = 101^\circ10'$) have been grown from the melt with crystal sizes of the order of $1 \times 0.25 \times 0.1$ mm$^3$ [9]. The corresponding pyroxene structure of monoclinic CoGeO$_3$ [10] consist of Co1 ions that are forming Co$_6$ octahedral zigzag chains running in c-direction, with adjacent Co$_2$ octahedra, compare Figure 1. The so formed Co ladders (or double-zig-zag chains) are separated by GeO$_4$ tetrahedra from each other. Throughout this article, we refer to the monoclinic form of CoGeO$_3$, which orders antiferromagnetically below $T_N \sim 36$ K [8].
Figure 1. Crystal structure of 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 cm$^3$-sized, as-grown single crystal of 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 twined 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 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 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 Co$^{2+}$ reference. The similarity of the Co-L$_{2,3}$ XAS spectra of CoGeO$_3$ and CoO, see Figure 4, reveals a Co$^{2+}$ high spin state in octahedral
coordination [11–13] in 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 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 CoGeO$_3$ single crystal.

The magnetic susceptibility $\chi$ of 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 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 CoGeO$_3$ is much larger than the theoretical spin-only value for Co$^{2+}$ ions of 3.87 $\mu_B$ and suggests that the 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$_3$ and of CoO at the Co L$_{2,3}$ edge.

Figure 5. (a) Direction dependent magnetic susceptibility ($\chi$) of CoGeO$_3$ single crystals measured in a field of $\mu_0 H = 0.1$ T. For comparison also the values for a CoGeO$_3$ 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 Kα radiation (Rietveld refinement with Fullprof [16]; χ² = 2.24). [*: unobserved reflections were also used.]

| Parameter                  | Value                      |
|----------------------------|----------------------------|
| Empirical formula          | CoGeO₃                     |
| Formula weight (g/mol)     | 179.5                      |
| Temperature                | room temperature           |
| Wavelength                 | Mo Kα                      |
| Crystal system             | monoclinic                 |
| Space group                | C 2/c (15)                 |
| Unit cell dimensions       | a = 9.6623(2) Å           |
|                           | b = 8.9928(2) Å           |
|                           | c = 5.16980(10) Å         |
|                           | β = 101.2785(10)°         |
| Volume                     | 440.535(16) Å³             |
| Z                          | 8                          |
| Density (g/cm³)            | 5.4134                     |
| Absorption coefficient µ   | 20.861                     |
| F(000)                     | 664                        |
| Crystal size               | ~10–20 μm                  |
| 2Θmax                      | 106.58°                    |
| Index range                | h: −21 → 21                |
|                           | k: −19 → 20                |
|                           | l: −11 → 10                |
| Reflections in total       | 13,219/2438                |
| Observed reflections       | 10,541/2078                |
| Internal R-value           | 2.31%                      |
| Completeness up to 2Θmax  | 91.48%                     |
| Absorption correction      | multi-scan                 |
| Min. / max. transmission   | 0.3738 / 0.7505            |
| Refinement method          | least squares on F²       |
| Reflections threshold *    | I > 5σ(I)                  |
| Goodness of fit            | 1.97                       |
| R / R_w                    | 1.63 / 5.28%               |
| Largest minima in Fourier  | −3.10 e⁻³ Å⁻³              |
| Largest maxima in Fourier  | 2.78 e⁻³ Å⁻³               |

Table 2. Refinement results of single crystal X-ray diffraction measurements of CoGeO₃. 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 | $U_{11}$ (Å$^2$) | $U_{22}$ (Å$^2$) | $U_{33}$ (Å$^2$) |
|------|----------------|----------------|----------------|
| 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 | $U_{12}$ (Å$^2$) | $U_{13}$ (Å$^2$) | $U_{23}$ (Å$^2$) |
|------|----------------|----------------|----------------|
| 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 CoGeO$_3$. BVS parameters were taken from Ref. [17].

| Atoms          | Distance (Å) / BVS |
|----------------|-------------------|
| Ge1-O1         | 1.7399 (14)       |
| Ge1-O2         | 1.7142 (14)       |
| Ge1-O3         | 1.7965 (18)       |
| Ge1-O3         | 1.7963 (15)       |
| BVS(Ge1)       | 3.896(8)          |
| 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)       |
| BVS(Co1)       | 1.999(3)          |
| Co2-O1         | 2.1229 (15)       |
| Co2-O1         | 2.1229 (15)       |
| Co2-O2         | 2.0157 (15)       |
| Co2-O2         | 2.0157 (15)       |
| Co2-O2         | 2.2588 (17)       |
| Co2-O2         | 2.2588 (17)       |
| BVS(Co2)       | 1.894(3)          |

3. Materials and Methods

The floating zone growth of monoclinic CoGeO$_3$ was carried out in a high pressure optical mirror furnace (HKZ, SciDre GmbH). Initially, Co$_3$O$_4$ and GeO$_2$ with an excess of 3% 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/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) 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 CoGeO$_3$ were initially studied using a SQUID magnetometer (MPMS-5XL, Quantum Design Inc.).

4. Conclusions

We have grown sizable single crystals of 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.

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