Floating-zone growth of large high-quality $CoAl_2O_4$ single crystals

A. Maljuk [a,*], V. Tsurkan [b,c], V. Zestrea [b], O. Zaharko [d], A. Cervellino [e], A. Loidl [c], D.N. Argyriou [a]

[a] *Helmholtz-Zentrum Berlin für Materialien und Energie, D-14109 Berlin, Germany*
[b] *Institute of Applied Physics, Academy of Sciences, MD-2028 Chisinau, R. Moldova*
[c] *Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, D 86159 Augsburg, Germany*
[d] *Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institute, CH-5232 Villigen, Switzerland*
[e] *Laboratory for Synchrotron Radiation II, Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen, Switzerland*

1. Introduction

Magnetic systems with frustrated exchange are intensively studied currently both theoretically and experimentally. A number of novel and exotic ground states, like spin-ice or spin-liquid were predicted and found recently [1,2]. Magnetic compounds AB_2X_4 with spinel structure are good candidates for observation of the frustration effects. Magnetic ions on the B-sites of the spinels form a network of corner-sharing tetrahedra, known as a most frustrated pyrochlore lattice [3]. Indeed, antiferromagnetic (AFM) spinels with the magnetic ions only on the B-sites reveal strong frustration effects resulting, for example, in composite spin degrees in cubic $ZnCr_2O_4$ [4], one half magnetization plateau in frustrated $CdCr_2O_4$ [5] or Peierls-like structural transitions attributed to a spin-driven Jahn–Teller effect [6–8]. Strong frustration effects were also found in a number of spinels containing magnetic ions solely on the A-sites [9,10]. They exhibit an extended range of the Curie–Weiss (CW) behavior of the magnetic susceptibilities down to very low temperatures and high values of the frustration parameter *f*, usually defined as the ratio of the CW temperature Θ_{CW} to transition temperature T_N, i.e. $f = |\Theta_{CW}|/T_N$. In $CoAl_2O_4$ spinel with the A-sites occupied by the high-spin ($S = 3/2$) Co^{2+}ions, magnetic and specific heat studies detected no long-range order down to 2 K despite the presence of strong AFM exchange interactions as indicated by their large negative CW temperature $\Theta_{CW} \sim -100$ K [10]. At temperatures below 5 K this compound undergoes short-range order exhibiting a spin-glass-like behavior. The resulting frustration parameter, $f = 22$, clearly indicates a strong magnetic frustration. Recent neutron-diffraction studies [11] revealed a liquid-like structural factor of the magnetic intensities and suggested a spin-liquid ground state for $CoAl_2O_4$. It has to be noted that all experimental studies of $CoAl_2O_4$ and related Co spinel compounds thus far were done on polycrystalline samples. This allowed one to get the information summed over reciprocal lattice vectors with the same length. To get more detailed insight on the spatial distribution of magnetic moments, and on dispersion of magnetic excitations, investigations on single crystals are highly necessary. This is particularly important in a view of elucidating the novel "spiral-spin liquid" ground state predicted recently for such frustrated magnets [12,13].

The $CoAl_2O_4$ compound has a high melting point of about 2000 °C. Only few attempts have been done before to grow this material. For example, small millimeter size single crystals of $CoAl_2O_4$ were obtained from PbO-PF_2 flux [14]. However, the size and volume of such crystals were not suitable for physical studies, like neutron scattering or optical measurements. Also, crystal contamination by flux and crucible material has to be taken into

---

[*] Corresponding author. Tel.: +49 30 8062 3079; fax: +49 30 8062 3172.
E-mail address: andrey.malyuk@hmi.de (A. Maljuk).

account. Larger crystals with volume up to 50 mm^3 were grown in [15] by the fusion in air. Unfortunately, no data concerning the crystal quality (mosaicity) were given in [14,15]. Moreover, the inversion degree, defined as Co to Al substitution, was not measured in these works. Here we report the first successful floating-zone growth of the high-quality $CoAl_2O_4$ single crystals with volume up to 1.0 cm^3. Details of the crystal growth, structural and magnetic characterization of the samples are given.

2. Experiment

As the starting material a polycrystalline powder of $CoAl_2O_4$ has been used. The powder was prepared by solid-state reaction from high purity (99.99%) binary oxides CoO and Al_2O_3. The synthesis was performed in alumina crucibles placed in evacuated quartz ampoules at a temperature of 1000 °C for 3 days. Then the ampoules were slowly cooled to room temperature with a cooling rate of 15 °C/h. Such sintering regime is essential to minimize the inversion disorder. The synthesis was repeated several times in order to reach better homogeneity and full chemical reaction of the starting oxides.

The pre-sintered powder was formed into cylindrical rods of 7–8 mm in diameter and 80–100 mm in length, and then pressed at a hydrostatic pressure of 3 kbar. The rods were sintered at 1300 °C for 24 h under argon flow. The heating and cooling rates were 150 °C/h. The apparatus used for the crystal growth was a four-mirror type infrared image furnace (Crystal System Inc. FZ-T-10000-H-III-VPR) equipped with four 1 kW halogen lamps as a heat source. The growth conditions were as follows: the seed and feed rods were rotated in opposite directions at 15–20 rpm; the traveling rate was 4 mm/h; $Ar/O_2 = 95/5$ flow was used.

Powder X-ray patterns of crashed single crystalline and polycrystalline materials have been collected at the Materials Science Beamtime (MSB) of Swiss Light Source (PSI, Switzerland). The wavelengths $\lambda = 0.495883$ for the single crystal and 0.414144 Å for the polycrystalline sample have been used to minimize absorption problem and to reach high $2\sin\theta/\lambda$ (>3 Å^{-1}). The powder was put inside 0.3 mm quartz capillaries, which were rotated at 30°/exposure for better powder average. The exposure time with the microstrip detector was 30 s.

Neutron-diffraction experiments have been performed on the TriCS instrument at the neutron spallation source SINQ (PSI, Switzerland). The neutrons with the wavelength $\lambda = 1.18$ Å have been used.

3. Results

Our preliminary experiments on powder samples show that one should use very low cooling rates, 50 °C/h and less, in order to minimize the chemical disorder (inversion degree) in the samples. It is well established that the inversion parameter strongly increases with temperature [16]. Therefore, on fast cooling the relaxation of ions between the tetrahedral and octahedral sites is limited leading to higher inversion degree [17]. The typical temperature gradients in the FZ growing crystal are 100–200 °C/cm. In this case the pulling rates of 3–4 mm/h correspond to the effective cooling rates of about 40–60 °C/h. Therefore, we never use the growth rates higher than 4 mm/h. Growth at 2 mm/h and less leads to the considerable material evaporation from the molten zone that makes difficult to maintain a stable zone.

The $CoAl_2O_4$ ingot grown at 4 mm/h is presented in Fig. 1. The crack-free boule with a metallic luster has 6.5 mm in diameter and over 40 mm in length. The grown ingot was cut into wafers perpendicular to the growth direction, and both surfaces of each wafer were polished to a mirror finish. The further study using optical polarized microscope (Leica DM EP) and X-ray Laue patterns (Fig. 2) verified that the end-portion of the ingot with the length over 30 mm was free from sub-grains and inclusions.

The neutron rocking curves of the $CoAl_2O_4$ sample with volume over 0.8 cm^3 are depicted in Fig. 3. The curves have a perfect shape without any shoulders also indicating the absence of sub-grains. The nuclear (2 2 0) and (2 2 2) reflections have the full-width at half-maximum (FWHM) of about 0.30 degree, which is the resolution limit of the instrument at the corresponding wavelength and scattering angle, proving the excellent quality of the grown crystal.

The X-ray diffraction patterns showed that all powder and single crystalline samples are single phase materials without any impurity phases. The X-ray data were analyzed by standard

Fig. 1. As-grown $CoAl_2O_4$ ingot, pulling rate 4 mm/h, the small gauge division is 1 mm.

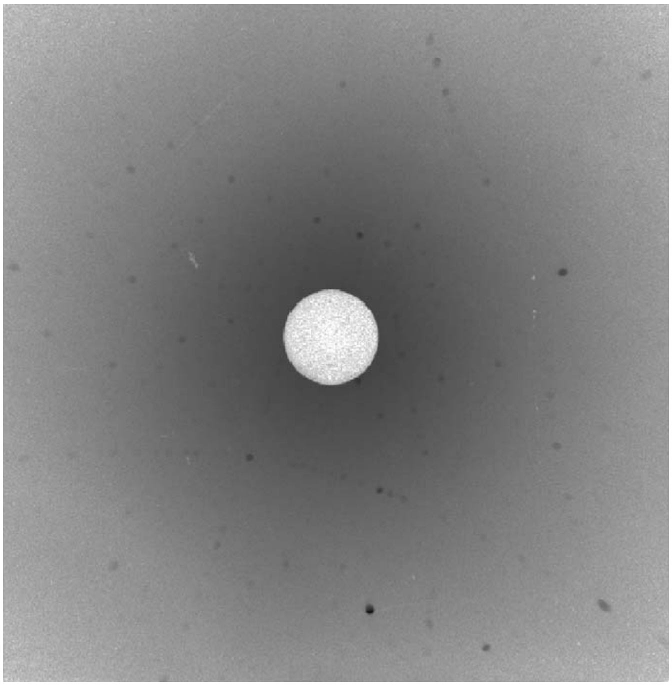

Fig. 2. Back-reflection Laue X-ray photograph of the as-grown $CoAl_2O_4$ single crystal.

Rietveld refinement using the FULLPROF program [18] assuming a cubic spinel structure with the space group $Fd\bar{3}m$ (No. 227). The following parameters have been fit: scale factor, zero point shift, resolution parameters, lattice constant, oxygen positional parameter, occupation factor of cations, and isotropic temperature factors for Co, Al and O ions. In the fitting procedure the occupation factor of oxygen was fixed to four, assuming that all positions are fully occupied and that the overall composition corresponds to stoichiometric $CoAl_2O_4$. The lattice constants a_0, the oxygen positional parameters x_O and the occupation factors for the Co and Al cations on the A- and B-sites are given in Table 1. Note that the inversion parameter, defined as $(1-Co/A)\times 100\%$, varies from 4% to 8% for the best polycrystalline samples known in literature [10,19]. Our as-grown $CoAl_2O_4$ single crystal has the inversion degree of about 8% from the X-ray refinement.

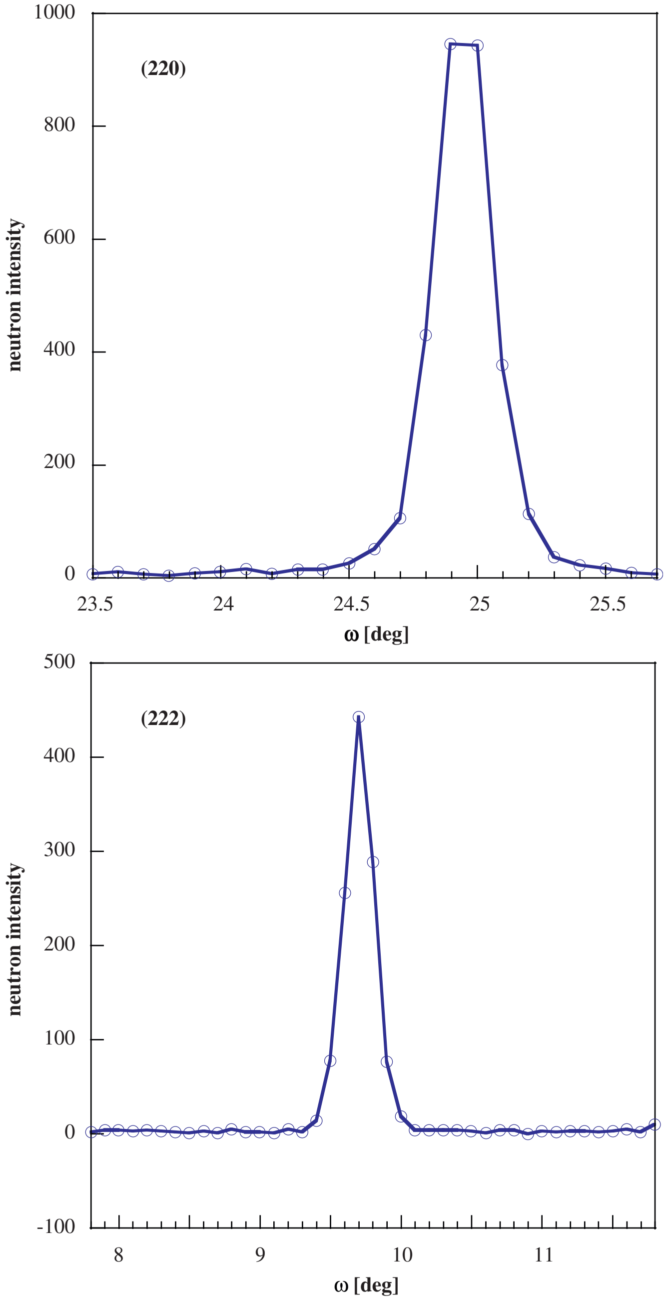

Fig. 3. Neutron rocking curves: (2 2 0) and (2 2 2) nuclear Bragg reflections.

Magnetic susceptibilities of the polycrystalline and single crystalline $CoAl_2O_4$ samples have been measured with a commercial SQUID magnetometer (MPMS-5, Quantum Design) in the temperature range $2\,K \leq T \leq 400\,K$. Fig. 4 presents the temperature dependences of the inverse molar susceptibilities $\chi^{-1} = (M/H)^{-1}$ of $CoAl_2O_4$ samples measured in an external magnetic field of $H = 10\,kOe$. The inverse susceptibility $\chi^{-1}(T)$ of both samples obeys a CW law for a temperature range above 50 K. The paramagnetic CW temperature Θ_{CW} and the effective magnetic moment μ_{eff} were determined from the CW fits to the experimental susceptibility $\chi(T)$ taking into account the diamagnetic corrections obtained from [10]. Table 2 summarizes the fit parameters, μ_{eff} and Θ_{CW}, obtained for the studied samples. The obtained value of the effective moment $\mu_{eff} = 4.63\,\mu_B$ for the single crystal is typical for the tetrahedral high-spin Co^{+2} ions, and is close to previously reported for powder samples [10]. We note a slight difference of the CW temperature for the studied samples

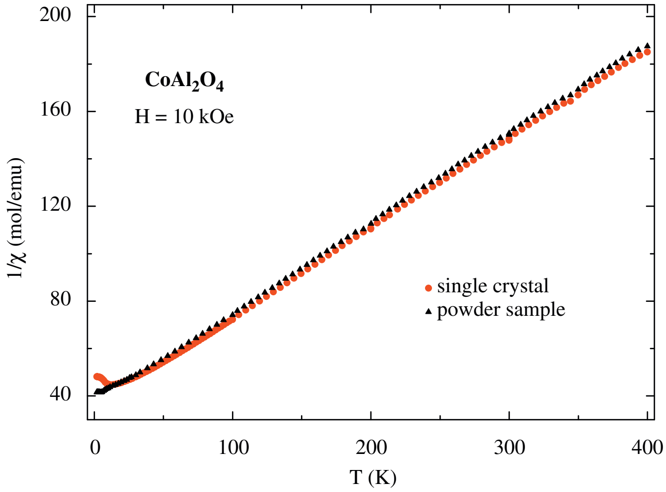

Fig. 4. Inverse molar susceptibility vs. temperature in a magnetic field of 10 kOe for polycrystalline and single crystalline $CoAl_2O_4$ samples.

Table 2
Curie–Weiss temperatures Θ_{CW} and effective moments μ_{eff} determined from the CW fits to the magnetic susceptibility of $CoAl_2O_4$ samples in the temperature range above 50 K.

Sample	Θ_{CW} (K)	μ_{eff} (μ_B)
Powder	−99(1)	4.62(2)
Crystal	−94(1)	4.63(2)

Table 1
Lattice constants a_0, oxygen positional parameter x_O in fractional coordinates (f.c.) and occupation factors of Co and Al cations on the A- and B-sites of $Co_{1-x}Al_x[Al_{2-x}Co_x]O_4$ obtained by Rietveld analysis.

Sample	a_0 (Å)	x_O (f.c.)	Co/A	Al/A	Al/B	Co/B	Rf	χ^2
Powder	8.10735(1)	0.26326(3)	0.830(1)	0.170(1)	1.830(1)	0.170(1)	5.8	2.4
Crystal	8.09853 (1)	0.26416 (4)	0.9206 (5)	0.0804 (5)	1.9206 (5)	0.0804 (5)	10.6	2.6

R factors and χ^2 values for each refinement are also indicated.

that can be probably attributed to difference in their inversion degree (17% for polycrystal and 8% for single crystal) as well as to possible oxygen defects.

4. Conclusions

Perfect $CoAl_2O_4$ single crystals with volume up to $1\,cm^3$ have been grown for the first time by crucible-free floating-zone technique. Neutron-diffraction experiments demonstrate the excellent quality of the grown crystals with mosaicity lower than 0.30. Lattice constant and inversion parameter are defined from the X-ray synchrotron measurements. The inversion degree of the single crystal (about 8%) is among the lowest reported so far for stoichiometric $CoAl_2O_4$. The paramagnetic CW temperature and the effective magnetic moment for the as-grown $CoAl_2O_4$ crystal have been obtained from the magnetization curves. Their values are close to those reported in literature for stoichiometric polycrystalline samples and typical for tetrahedral high-spin Co^{2+} ions.

Acknowledgements

The authors thank Mrs. Dana Vieweg for the experimental support. The support of PSI via collaborative grant MOP1-33010-CH-08 of the GAP of the US CRDF is gratefully acknowledged.

References

[1] A.P. Ramirez, A. Hayashi, R.J. Cava, R. Siddhartan, B.S. Shastry, Nature (London) 399 (1999) 333.
[2] S.T. Bramwell, M.J.P. Gingras, Science 294 (2001) 1495.
[3] P.W. Anderson, Phys. Rev. 102 (1956) 1008.
[4] S.-H. Lee, C. Broholm, W. Ratcliff II, G. Gasparovic, Q. Huang, T.H. Kim, S.-W. Cheong, Nature (London) 418 (2002) 856.
[5] H. Ueda, H.A. Katori, H. Mitamura, T. Goto, H. Takagi, Phys. Rev. Lett. 94 (2005) 047202.
[6] S.-H. Lee, C. Broholm, T.H. Kim, W. Ratcliff II, S.-W. Cheong, Phys. Rev. Lett. 84 (2000) 3718.
[7] J. Hemberger, T. Rudolf, H.-A. Krug von Nidda, F. Mayr, A. Pimenov, V. Tsurkan, A. Loidl, Phys. Rev. Lett. 97 (2006) 087204.
[8] O. Tchernyshyov, R. Moessner, S.L. Sondhi, Phys. Rev. B 66 (2002) 064403.
[9] V. Fritsch, J. Hemberger, N. Büttgen, E.-W. Scheidt, H.-A. Krug von Nidda, A. Loidl, V. Tsurkan, Phys. Rev. Lett. 92 (2004) 116401.
[10] N. Tristan, J. Hemberger, A. Krimmel, H.-A. Krug von Nidda, V. Tsurkan, A. Loidl, Phys. Rev. B 72 (2005) 174404.
[11] A. Krimmel, V. Tsurkan, D. Sheptyakov, A. Loidl, Physica B 378–380 (2006) 583.
[12] D. Bergman, J. Alicea, E. Gull, S. Trebst, L. Balents, Nature Phys. 3 (2007) 487.
[13] S.B. Lee, L. Balents, Phys. Rev. B 78 (2008) 144417.
[14] K. Toriumi, M. Ozima, M. Akaogi, Y. Saito, Acta Cryst. B 34 (1978) 1093.
[15] N.G. Matveeva, A.I. Shelykh, Phys. Stat. Sol. (b) 50 (1972) 83.
[16] Hugh St.C. O'Neill, Eur. J. Mineral. 6 (1994) 603.
[17] S. Greenwald, S.J. Pickart, F.H. Grannis, J. Chem. Phys. 22 (1954) 1597.
[18] J. Rodriguez-Carvajal, Physica B 192 (1993) 55.
[19] T. Suzuki, H. Nagai, M. Nohara, H. Takagi, J. Phys.: Condens. Matter 19 (2007) 145265.