Magnetic structure and its temperature for $CoCr_2Se_4$

V. Svitlyk[1], L.M.D. Cranswick[2], and Y. Mozharivskyj[1]
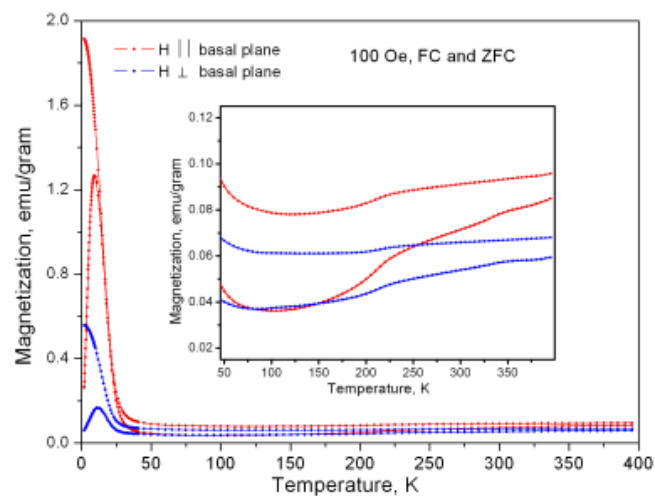
[1] Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

[2] Canadian Neutron Beam Centre, NRC, Chalk River Laboratories, Chalk River, ON, Canada K0J 1J0

$CoCr_2Se_4$ adopts a Cr_3Se_4-type structure, which is also known as a filled CdI2 structure [1]. The magnetic studies performed on powders almost 40 years ago suggest antiferromagnetic ordering around 190-210 K [2]. However, our magnetic data (see below) both on powders and single crystals suggest that magnetic ordering is unlikely to be entirely antiferromagnetic and, besides, it persists to at least 700 K.

Since a $CoCr_2Se_4$ is reported to be a semiconductor [3,4] (we will be verifying its electrical conductivity), our magnetic data suggest that $CoCr_2Se_4$ is likely to be a magnetic semiconductor with relatively high ordering temperature. A family of magnetic semiconductors is rather small and, besides, almost none of them is magnetically ordered above RT. Magnetic semiconductors hold a potential for spintronic applications, but progress is hindered by the absence of magnetic semiconductors that can function at RT.

Magnetisation. Contrary to previous magnetic studies that suggest simple antiferromagnetic ordering in $CoCr_2Se_4$ powders, [2] our magnetic data (Figure 1) on single crystals indicate that the magnetic ordering is not fully antiferromagnetic and, besides, it persists to at least 700 K. In fact, large magnetisation values and hysteresis at room temperature and 4 K suggest the presence of a ferro- or ferrimagnetic-type ordering at both temperatures (Figure 2). The saturation moments achieved in the 7 T magnetic field are 1.2 μ_B/f.u. and 0.26 μ_B/f.u. at 4 K and 300 K, respectively, which are relatively low considering the d^7 and d^3 configurations of Co^{2+} and Cr^{3+} in $CoCr_2Se_4$. There is also a spin-glass transition below 25K.

It can be speculated that the magnetic behaviour of $CoCr_2Se_4$ stems in part due to superparamagnetic Co impurities. However, (1) if the ferromagnetic-type behavior of $CoCr_2Se_4$ were due to the superparamagnetic Co nanoparticles, then the concentration of Co nanoparticles would have to be in excess of 10 wt. %, based on the value of saturation magnetisation at 4 K. However, no Co nanoparticles were detected on the surface of the single crystals (from the SEM analysis), and inclusion of such quantities into the bulk of single crystals is very improbable. (2) The observed magnetic anisotropy is incompatible with the superparamagnetic impurities, which should display an isotropic behaviour, and thus it has to be intrinsic to the phase.
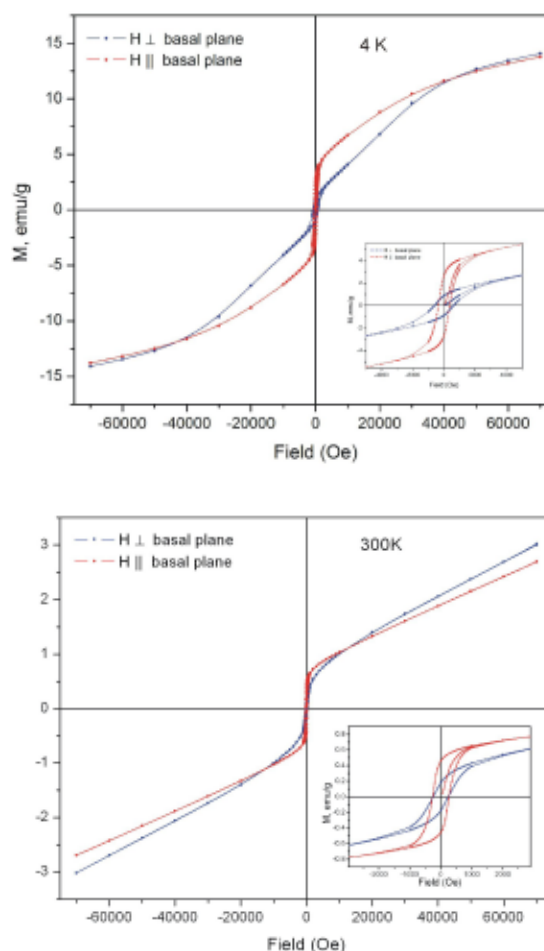
Fig. 2 Magnetisation vs. field for a CoCr2Se4 single crystal at 4 K and 300 K.

Synthesis and X-ray structure analysis. Starting materials were powders of Co (99.8%, CERAC), Cr (99.95%, CERAC) and Se (99.99%, Alfa Aesar). Powders with the $CoCr_2Se_4$ composition and the total mass of 1 gram were mixed and pressed in an Ar-filled dry box. All subsequent handling was also

Fig. 1 Magnetisation vs. temperature for a $CoCr_2Se_4$ single crystal.

performed in the dry box. The pallet was sealed in the evacuated silica tubes, treated at 800°C for 50 hours. After being quenched in cold water, the sample was re-ground, pressed, sealed in the evacuated silica tubes and annealed at 800°C for 2 weeks, followed by quenching in cold water. After this treatment, the $CoCr_2Se_4$ sample was again heated to 800°C, annealed for 4 hours at this temperature and cooled at the rate of 15°C/hour to room temperature.

Room-temperature (RT) X-ray powder diffraction pattern in the 20–90° 2θ range were recorded on a PANalytical X'Pert Pro diffractometer with an X'Celerator detector and a $CuK_\alpha1$ radiation. The full-profile Rietveld refinement (Rietica program [5]) was used for phase analyses, to derive lattice constants and refine atomic parameters (Table 1-2).

Table 1.

Powder refinement data for the CoCr2Se4 sample.

Sample	$CoCr_2Se_4$
Lattice parameter, Å	a = 13.0192(2) b= 3.60728(5) c = 6.25614(8) β = 117.7941(6)
Volume, Å3	259.916(6)
Z	2
Reflections	132
Atomic param. refined	11
R_I	0.039
R_p	0.059
R_{wP}	0.078

$R_I = \Sigma\,|\,I_o\text{-}I_c\,|\,/\,\Sigma\,|\,I_o\,|\,,\ R_P = \Sigma\,|\,y_{oi}\text{-}y_{ci}\,|\,/\,\Sigma\,|\,y_{oi}|,\ R_{wP}=(\Sigma w_i(y_{oi}\text{-}y_{ci})^2/\Sigma w_i(y_{oi})^2)^{1/2},\ w_i = (y_{oi})^{-1/2}.$

Table 2.

Atomic and isotropic temperature (U) parameters for $CoCr_2Se_4$

Atom		Occupancy	x/a	y/b	z/c	U (Å²)
Co	2a	1	0	0	0	0.4(1)
Cr	4i	1	0.2584(4)	0	0.2875(7)	0.72(8)
Se1	4i	1	0.3656(2)	0	0.0265(5)	0.57(9)
Se2	4i	1	0.1198(2)	0	0.4523(5)	0.24(8)

Neutron powder diffraction data. The neutron diffraction data were obtained on the C2 diffractomter before an NRU reactor, Chalk River, in the 3.303-83.397° 2θ range with 0.1002425° step and within the 3.8-293 K temperature range.
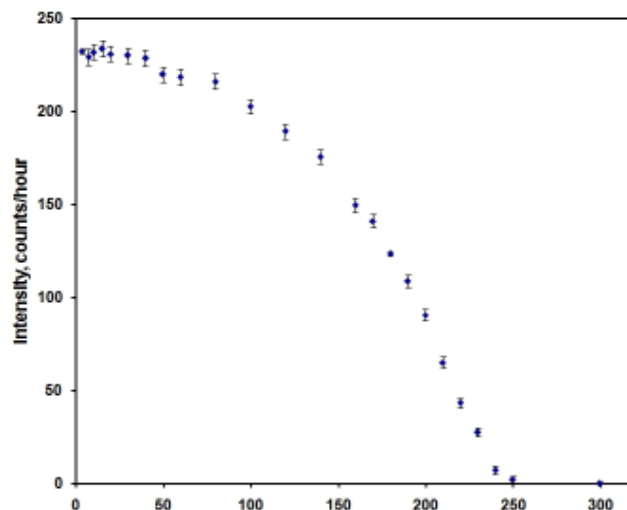

Fig. 3 *Integrated intensity of the magnetic peak at 2θ = 21.2° as a function of temperature.*

The neutron powder diffraction data indicate an onset of the antiferromagnetic ordering below T_N = 250 K (Figure 3), which coincides with a step in magnetisation (Figure 1). Integrated intensities for the magnetic peak at 2θ of 21.2° in Figure 3 were generated by the XFIT software 6.

The magnetic structure of $CoCr_2Se_4$ (Figure 4) was refined using the FULLPROF software package [7]. The long-range ordering of the magnetic moments is antiferromagnetic below the ordering temperature (Figure 5). The refined magnetic moments for Cr and Co at 3.8 K are 1.37 and 1.03 μ_B which are much smaller than the spin-only saturation magnetic moments of 3 μ_B for Cr^{3+} (d^3 configuration) and Co^{2+} (d^7 high-spin configuration).

While the neutron diffraction data neither provide information regarding the nature of interactions at room temperature nor shed a light on high values of magnetisation below T_N, they are an important step in understanding the unusual magnetic behavior of $CoCr_2Se_4$.
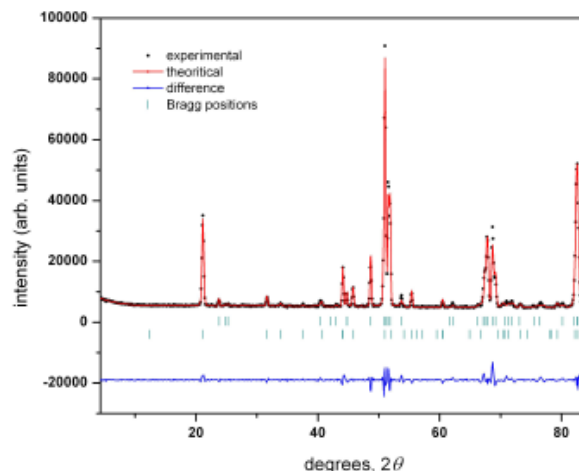
Fig. 4 *Refinement of the neutron powder diffraction data for $CoCr_2Se_4$ at 3.8 K.*
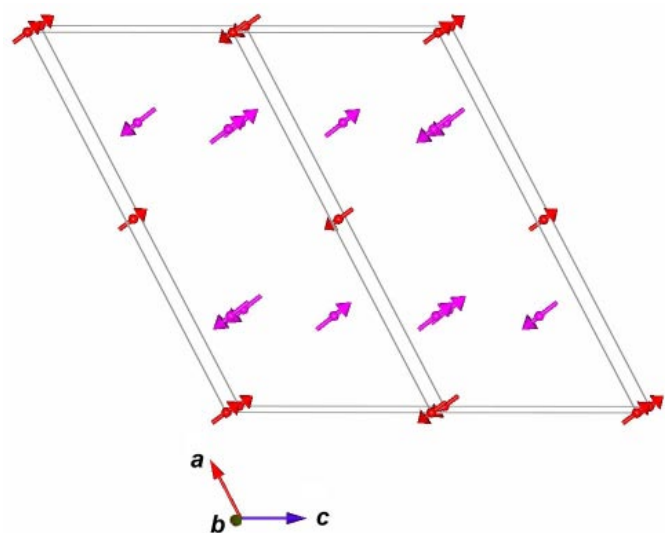
Fig. 5 Magnetic structure of $CoCr_2Se_4$ at 3.8 K. Co moments are in red, Cr moments are in violet.

References

[1] Smirnov, S. G.; Rozantsev, A. V.; Kesler, Y. A.; Gordeev, I. V.; Tret'yakov, Y. D. Izv. Akad. Nauk SSSR, Neorg. Mater. 1983, 19, 886-888.

(2) Morris, B. L.; Russo, P.; Wold, A. J. Phys. Chem. Solids 1970, 31, 635-638.

(3) Maciazek, E.; Molak, A.; Goryczka, T. J. Alloys Compd. 2007, 441, 222-230.

(4) Snyder, G. J.; Caillat, T.; Fleurial, J. P. Materials Research Society Symposium Proceedings 1999, 545, 333-338.

(5) Hunter, B. A.; Howard, C. J. Rietica; Australian Nuclear Science and Technology Organization: Menai, Austalia, 2000.

(6) Cheary, R. W.; Coelho, A. A. Programs XFIT and FOURYA, deposited in CCP14 Powder Diffraction Library, Engineering and Physical Sciences Research Council, Daresbury Laboratory, Warrington, England. (http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm)] 1996.

(7) Rodriguez-Carvajal, J. IUCR Newsletter 2001, 26, 12-19.