

## Frustrated Triangular Lattice Magnetism in Delafossite Type Yb- and Cr-based Systems

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**4f-ion-based triangular lattices of the delafossite structure have now established themselves as an emerging research field in their own right. Among the 4f-ions, Ytterbium is the Kramers ion with the smallest ionic radius so that it can be easily inserted into the cage of the chalcogenides. The magnetic exchange between the Kramers ions takes place via the *p*-orbitals of the chalcogenides and, in contrast to *d*-ions, it is bond-dependent which originates from the complex 4f-ground state wave function of the lowest Kramers doublet. This leads to a strong frustration in NaYbCh<sub>2</sub> (Ch: O, S, Se) and the formation of the spin liquid ground state [1]. To further explore this interesting class of materials, we have now pursued the various directions: i) variation of the monovalent ion (Na replaced by Tl with much larger ionic radius), ii) exploration of systems with other Kramers ions (like Er) or non-Kramers ions (like Tm) and replacement of Yb by Gd (here spin orbital interaction is absent) and iii) diluted systems like Na(Yb,Lu)S<sub>2</sub>. The latter system will be discussed in more detail below. Another route is the study of chromium non-oxy delafossites. While Cr oxy delafossites have already been sufficiently investigated, there is still little research in this area. AgCrSe<sub>2</sub> in particular is of interest here as it is semi metallic and shows a planar cycloidal magnetic order that emerges out of a strongly frustrated state. This state is characterized by anisotropic and possibly chiral fluctuations. Starting from this material, the research field was extended to isostructural AgCrS<sub>2</sub> and the related system Cr<sub>3</sub>Se<sub>4</sub>.**

Yb-based magnets, with a perfect triangular lattice of pseudospin  $\frac{1}{2}$  Yb<sup>3+</sup> ions, have emerged as candidates for realizing a quantum spin-liquid state, with NaYbS<sub>2</sub> being a prominent example [1, 2, 3]. The solid-solution series NaYb<sub>1-x</sub>Lu<sub>x</sub>S<sub>2</sub> was established, where Yb and Lu occupy the B-site of the 3R  $\alpha$ -NaFeO<sub>2</sub> structure statistically [4]. The lattice parameters of the series ideally follow Vegard's rule, and neither evidence for a phase segregation nor for an ordered superstructure was found. It was possible to grow very homogeneous crystals in the substitution series (Figure 1a, b). The crystal growth was carried out at the TU Dresden in the inorganic chemistry department as part of the SFB 1143 ("correlated magnetism: from frustration to topology") project. Since the crystals are too small for conventional SQUID magnetometry, the ESR intensity was used as local susceptibility. The ESR susceptibility  $\chi_{ESR}$  could be nicely fitted with a Curie-Weiss (CW) law  $\chi_{ESR} \propto 1/(T-\theta)$  with negative Weiss temperatures  $\theta$ .  $\chi_{ESR}(T)$  was determined by integrating the ESR lines in the entire magnetic field range (Figure 1d). Upon increasing the Lu concentration, the Weiss temperature  $\theta$  decreases in a linear fashion (Figure 1c). This indicates clearly that the magnetic exchange network of NaYbS<sub>2</sub>, especially the strength of spin correlations, can be tuned by a random Lu substitution on the Yb-site while maintaining the strong frustration and possibly preserving the spin liquid ground state. Additional ZFC/FC magnetization measurements clearly rule out

spin glass type of behavior and/or short-range order hysteresis effects [4]. This verifies the entanglement between the spins in the Heisenberg triangular lattice, a prerequisite for a 4f-spin liquid, and the absence of strong dipolar coupling.

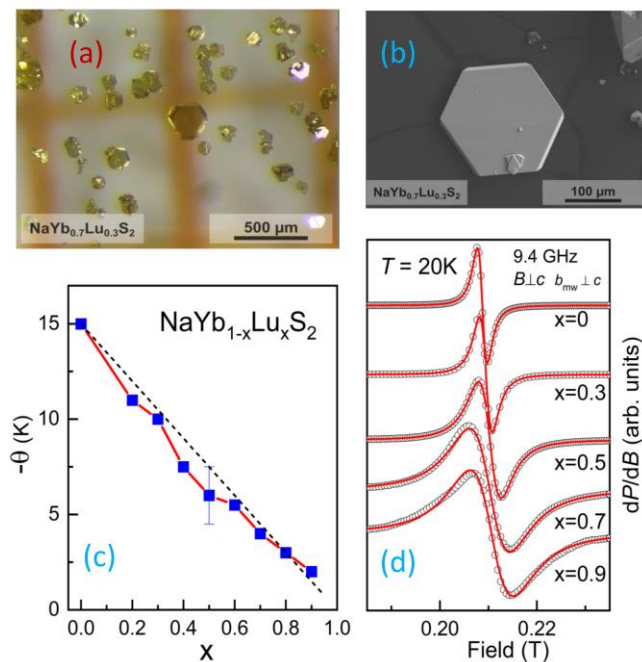


Fig. 1: Images of crystals taken under an optical microscope (a) and by scanning electron microscopy (b). Weiss temperature vs. Lu concentration determined by ESR measurements (c). Typical X-band ESR spectra at  $T = 20$  K of Yb<sup>3+</sup> for selected Lu concentrations (d) [4].

Most of the research on  $3d$ -ion delafossites done so far was on oxygen-based delafossites (DFs) whereas non-oxygen DFs (with S, Se or Te) have been less investigated. The variation of the ionic radii of the mono- and trivalent- ions has only a little effect on the band structure and mainly tunes the lattice parameters whereas the choice of the chalcogenide ion itself has a strong impact on the band structure. For example, the oxy delafossite  $\text{PdCoO}_2$  has a quasi two-dimensional conductivity and the density of states at the Fermi level shows minor chalcogenide  $2p$ -electron admixture. In contrast to that in  $\text{AgCrS}_2$  or  $\text{AgCrSe}_2$  the larger spatial extended  $3(4)p$ -states of S and Se promote the emergence of hybridized  $p$ -states at the Fermi level which finally leads to three-dimensional metallic or semi-metallic conductivity (see [PQM\\_09\\_Rosner](#)). This promotes correlation effects in general, and together with the emergence of strong spin polarization, unconventional magnetism and (magneto-) transport is expected.

While studies on magneto-transport are the subject of another highlight report ([PQM\\_07\\_Zhang](#)), in the following chapter we report in detail on the unconventional magnetism of  $\text{AgCrSe}_2$  single crystals. As already mentioned, there were only a few results on  $\text{AgCrSe}_2$  single crystals at the beginning of the investigation. We succeeded in growing these single crystals by chemical vapor transport (CVT) at the MPI CPFS and in an iterative process we managed to optimize the growth in terms of homogeneity and crystal size (Figure 2).

There are other important points to motivate our study of the magnetic phase diagram, namely: whereas the Cr-oxygen delafossites crystallize in the  $R\bar{3}m$  space group and are characterized by a very strong AFM

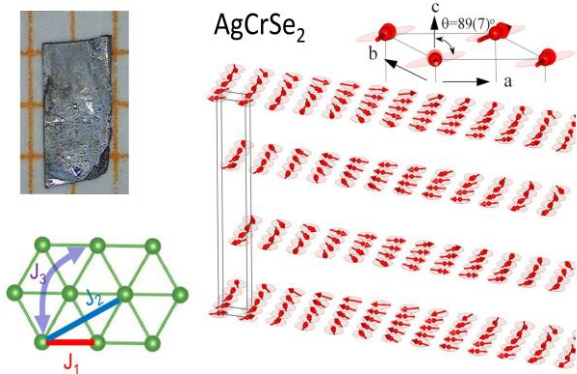


Fig. 2:  $\text{AgCrSe}_2$  single crystal (top, left). The lateral extension corresponds to the  $(a,b)$  plane and the direction perpendicular to it is the  $c$  axis. Schematic representation of the long-period modulated magnetic structure of the cycloidal order in  $\text{AgCrSe}_2$  (right). Heisenberg type 2D exchange model for the triangular lattice (bottom, left) [5].

nearest-neighbour interaction  $J_1$  (Figure 2) which then usually leads to very robust planar  $120^\circ$  spin order, the Cr-sulfide and Cr-selenide delafossites display transitions from the  $R\bar{3}m$  space group to the lower symmetry  $R3m$  space group. Therefore, asymmetric exchange interactions between the Cr ions are possible which allows, in addition to the Heisenberg superexchange and a possible weak Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange, for a sizable Dzyaloshinskii-Moriya (DM) interaction between the magnetic ions. First detailed neutron scattering experiments on  $\text{AgCrSe}_2$  polycrystals at ISIS Neutron and Muon Source (UK) in the zero magnetic field show a cycloidal planar magnetic order (sketched in Figure 2) with propagation vector  $k = (0.037, 0.037, 3/2)$  and the presence of strong fluctuations existing up to high temperatures. There was no evidence of a sizable DM-interaction. However, recent measurements on single crystals in cooperation with the TU Dresden at the PSI (Villigen, Switzerland) indicate that the DM interaction plays a role in the magnetic field.

Figure 3 shows the magnetic susceptibility of  $\text{AgCrSe}_2$  as a function of temperature in a magnetic field of 1 T applied in the  $(a,b)$ -plane ( $H \perp c$ ) and in the  $c$ -direction  $H \parallel c$ . Below the ordering temperature of  $T_N \approx 32$  K a strong magnetic anisotropy is observed. Above  $T_N$ , the magnetic anisotropy disappears and a pronounced maximum at  $T^* = 46.3$  K is found. Above 150 K, the

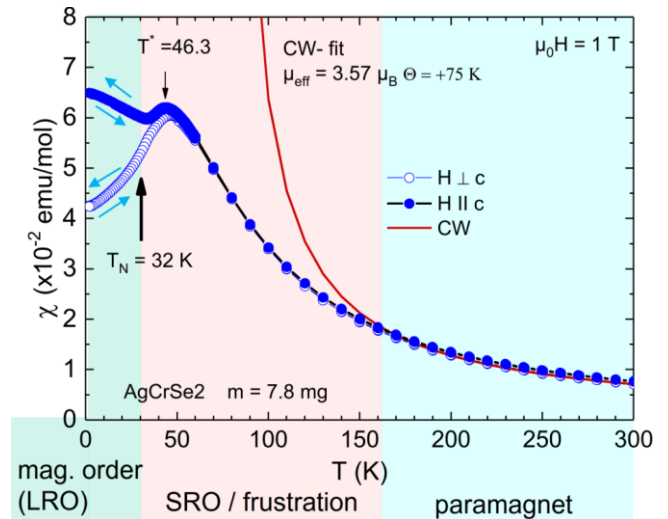


Fig. 3: Temperature dependence of the magnetic susceptibility of  $\text{AgCrSe}_2$  measured at  $\mu_0 H = 1$  T for fields  $H \perp c$  and  $H \parallel c$ . The solid line corresponds to a Curie-Weiss fit. The three main temperature ranges are characterized by i) paramagnetic behavior, ii) the occurrence of strong frustration with possible short-range fluctuating regions (SRO) and iii) the long-range magnetic cycloidal order (LRO) [5].

susceptibility can be well fitted by a Curie-Weiss (CW) law, yielding a positive Weiss temperature of  $\theta = +75$  K and an effective moment of  $\mu_{eff} = 3.57 \mu_B/\text{Cr}$ . This value of  $\mu_{eff}$  is slightly smaller than the theoretical prediction for the spin-only value of trivalent Cr ( $3d^3$ ) with  $S = 3/2$  and  $\mu_{eff} = 3.87 \mu_B$ .

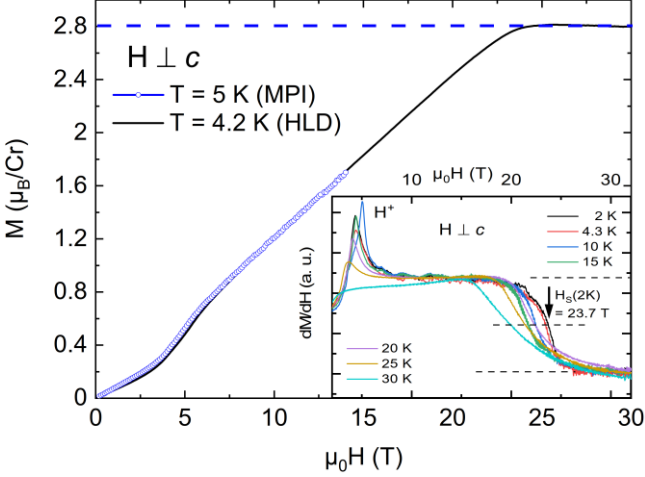


Fig. 4: Magnetization versus field for  $H \perp c$ . Open symbols represent data from measurements in static fields in a PPMS and solid lines high field magnetization data obtained in pulsed fields at the HLD. The inset shows the first field derivative of the magnetization versus field for  $H \perp c$  at various temperatures. The metamagnetic transition at  $H^+$  is defined by a peak, whereas the onset of saturation at  $H_S$  is given by a step in the derivatives [5].

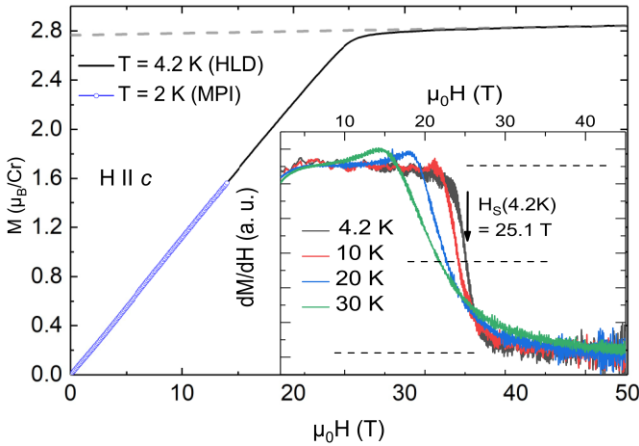


Fig. 5: Magnetization versus field for  $H \parallel c$ . Open symbols represent PPMS data and solid lines represent high field data obtained in pulsed fields. The dashed line corresponds to the linear in field Van Vleck contribution (above 40 T with  $\chi_{VV} = 0.0008 \text{ emu/mol}$ ). The inset shows the first field derivative of the magnetization versus field at various temperatures. The saturation field  $H_S$  is given by a step in the derivatives [5].

The magnetization  $M(H)$  was measured for  $H \perp c$  (Figure 4) and  $H \parallel c$  (Figure 5) in fields up to 14 T using the dc-magnetometer-option in the PPMS and in a susceptometer setup in pulsed magnetic fields up to 50 T at the Dresden High Field Laboratory (HLD). For  $H \perp c$  a field-induced metamagnetic transition at  $H^+(5 \text{ K}) = 5 \text{ T}$  in  $M(H)$  is followed by a saturation of the magnetization at  $M_S = 2.8 \mu_B/\text{Cr}$  above  $H_S = 23.7 \text{ T}$  (Figure 4). The crossover to saturation at high fields is broadened toward higher temperatures. We use the half height of the high field step in the first derivative as a measure for the transition to saturation (see inset Figure 4 and Figure 5). From the ESR an isotropic saturation magnetization of about  $M_S = gJ = 3 \mu_B/\text{Cr}$  is expected for  $J = 3/2$  and  $g = 2$ . The experimentally determined saturation magnetization of  $2.8 \mu_B/\text{Cr}$  does not fully reach the value predicted by the ESR. Possible reasons for that might be an orbital moment contribution, in addition to the spin-only moment, or shielding effects from itinerant conduction electrons with admixed Cr- $3d^3$  character.

Figure 6 shows the  $H$ - $T$  phase diagram of  $\text{AgCrSe}_2$  for both directions,  $H \perp c$  and  $H \parallel c$ . The experimentally established  $H$ - $T$  phase diagram is consistent with a planar Heisenberg model, in which the nearest-neighbor interaction, unlike in the Cr-oxygen delafossites, is ferromagnetic and the third-nearest-neighbor interaction is antiferromagnetic. In  $\text{AgCrSe}_2$  the interactions among the Cr ions have just the right strength to be tuned by experimentally accessible

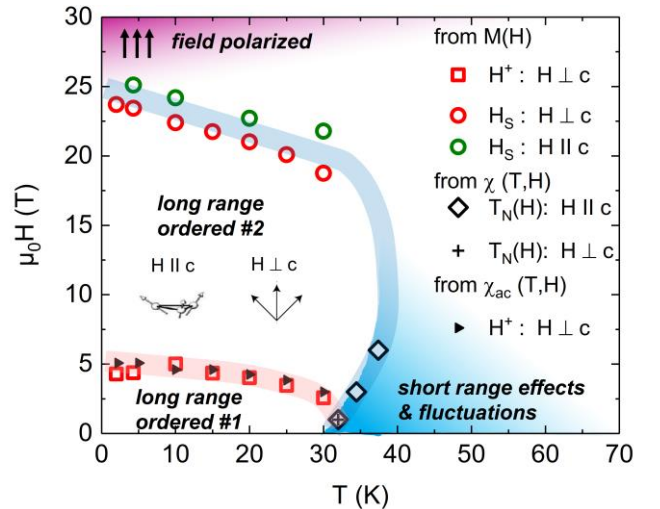


Fig. 6:  $H$ - $T$  phase diagram of  $\text{AgCrSe}_2$ , obtained from various methods for magnetic fields  $H \perp c$  and  $H \parallel c$ . The ordered state #1 represents the cycloidal phase for  $H \perp c$  below  $H^+(T)$ , whereas phase #2 represents a planar fan-like phase for in-plane fields (above  $H^+(T)$ ) and a more cone-like phase for fields in  $c$ -direction [5].

magnetic fields. In this respect, AgCrSe<sub>2</sub> is a model system for the study of a planar Cr<sup>3+</sup> triangular lattice with dissimilar Heisenberg-like interactions. In addition to the magnetic phase diagram, the band structure was calculated in great detail for the entire series AgCrCh<sub>2</sub> (Ch: S, Se, Te) (see [PQM\\_09\\_Rosner](#)). The results are in good agreement with the photoemission data obtained [5, 6]. As already mentioned, neutron measurements in magnetic fields on the single crystals are in progress which indicate a rather complex behavior in fields of a few tesla in the ordered state which might support the presence of chiral spin textures [7]. The observed unconventional anomalous Hall effect in the ordered state may also be related to this [8]. Furthermore, a Kondo scenario is also being discussed as an explanation for the magnetotransport in the vicinity of the magnetic order [9]. Crystal growth of AgCrS<sub>2</sub> has been achieved (by CVT) and first investigations show an antiferromagnetic stripe ordering accompanied by a change in the crystal structure. Furthermore, the related binary system Cr<sub>3</sub>Se<sub>4</sub> was successfully grown in single crystal form (by CVT), which also shows the coexistence of ferromagnetic and antiferromagnetic interactions. In this respect, we can expect some interesting results from the class of binary and ternary non-oxy chromates in the future.

### External Cooperation Partners

Th. Doert (Technical University Dresden (TUD, Germany)); D. Inosov and A. Sukhanov (TUD, Germany); H. Kühne (High Field Laboratory, Rossendorf, Germany); P. King (University of St Andrews, United Kingdom); P. Manuel and D. Khalyavin (ISIS Neutron and Muon Source, United Kingdom); A. Strydom (University of Johannesburg, South Africa); S. Nikitin (Paul Scherrer Institut, PSI, Switzerland); M. Vojta (TUD, Germany); G. Vinai and V. Polewczyk and P. Torelli (Istituto Officina dei Materiali (IOM)-CNR, Trieste, Italy); J. Wosnitza (High Field Laboratory Rossendorf & TUD, Germany).

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