# Understanding magnetic properties of $M \text{CrS}_2$ (*M*=Li, Na, K, Cu, Ag)

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# Outline

**Motivations** 

**Crystal and electronic structures** 

**Magnetic interactions between Cr spins** 

Conclusions



Magnetic Cr ions on a triangular lattice  $\downarrow\downarrow$ geometrical frustrations  $\downarrow\downarrow$ unusual magnetic properties







J < 0: frustrated ground state with 120° spin structure ( $\vec{S}_1 + \vec{S}_2 + \vec{S}_3 = 0$ )

# **3D pyrochlor lattice**



e.g.

- pyrochlor compounds
- spinels (MCrX<sub>2</sub>)

All configurations with  $\vec{S_1} + \vec{S_2} + \vec{S_3} + \vec{S_4} = 0$  are degenerate





## competing interactions

a linear chain of classical spins  $\vec{S}$  with AFM nn  $J_1$  and nnn  $J_2$  interactions:

Energy:  $E = S^2(J_1 \cos \phi + J_2 \cos 2\phi)$ 

where  $\phi$  is the angle between the neighbouring spins

#### competing interactions



# Multiferroics (magnetism vs. ferroelectricity)

magnetism ( $d^n$ ) or ferroelectricity ( $d^0$ ,  $d^{10}$ )

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↓
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non-collinear spin-spiral magnetic structure

\downarrow\downarrow

broken inversion symmetry

\downarrow\downarrow

multiferroicity (TbMnO<sub>3</sub>, CoCr<sub>2</sub>O<sub>4</sub>)
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D.I. Khomskii, JMMM 306, 1 (2006)

## **AgCrS**<sub>2</sub>: A Spin Driven Ferroelectric

K. Singh, A. Maignan, C. Martin, and Ch. Simon, Chem. Mater. 21, 5007 (2009)



- magnetic order below  $T_N$ =42 K
- anomaly of the dielectric permittivity at  $T_N$
- electrical polarization vanishes above  $T_N$
- P decreases as H increases



## Unconventional magnetic order in AgCrS<sub>2</sub>



- rhombohedral  $(R3m) \rightarrow$  monoclinic (Cm) transition at  $T_N$
- split nn Cr-Cr distances
- double stripe AFM magnetic order in the ab plane

$$E_{ds} = JS^2$$
  $E_{FM} = 3JS^2$   $E_{120^\circ} = \frac{3}{2}JS^2$   
F. Damay, *et al* PRB **83**, 184413 (2011)

A surprising variety of magnetic phases:

- LiCrS<sub>2</sub>: 120° AFM order in the ab plane; AFM along c ( $T_N$ =55 K)
- NaCrS<sub>2</sub>: non-collinear spin-spiral structure ( $T_N$ =19 K)
- KCrS<sub>2</sub>: FM in the ab plane; AFM along c ( $T_N$ =38 K)
- CuCrS<sub>2</sub>: non-collinear spin-spiral structure ( $T_N$ =39 K)
- AgCrS<sub>2</sub>: AFM double stripe; AFM along c ( $T_N$ =42 K)
- AuCrS<sub>2</sub>: AFM double stripe structure ( $T_N$ =55 K)

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Can we understand this sequence of magnetic orders?

## **Crystal structures**



- triangular  $CrS_2$  layers with abc stacking separated by M layers
- trigonally distorted CrS<sub>6</sub> octahedra (trigonal anti-prisms)
- Li, Na, K:  $MS_6$  anti-prisms; Cu, Ag:  $MS_4$  pyramids; Au: AuS<sub>2</sub> dumbbells
- AgCrS<sub>2</sub> and CuCrS<sub>2</sub>: non-centrosymmetric R3m structure with two S ions

## **Bond lengths**

M	group	$d_{ m CrCr}$ (Å)	$d^{av}_{ m CrS}$ (Å)	Cr-S-Cr angle	ab magnetic order
Li	$P\overline{3}m1$	3.4515	2.4063	91.7	$120^{\circ} \text{ AFM}$
Na	$R\bar{3}m$	3.5561	2.4249	94.3	spin spiral
K	$R\bar{3}m$	3.6010	2.4123	96.6	FM
Cu	R3m	3.4728	2.4036	90.6, 94.6	spin spiral
Ag	R3m	3.4979	2.4085	92.2, 94.1	AFM double stripes
Au	$R\bar{3}m$	3.4826	2.3862	93.7	AFM double stripes

- $d_{\rm CrS}^{av}$ , i.e. CF splitting, does not change much
- $d_{\rm CrCr}$  increases from 3.4515 Å in Li to 3.6010 Å in K
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Magnetic order changes from 120° AFM to FM with the increase  $d_{\rm CrCr}$ 

 $\operatorname{Ag}^{1+}\operatorname{Cr}^{3+}\operatorname{S}_2^{2-} \Rightarrow \operatorname{Ag} d^{10}s^0$ ,  $\operatorname{Cr} d^3$ ,  $\operatorname{S} p^6$ 



- S 3s and 3p completely filled
- Ag 4d filled; Ag 5s empty



Hund's coupling:

•  $J_H$ : Cr  $d \to d_{\uparrow} + d_{\downarrow}$ 

crystal field:

- $\Delta_{cub}$ : Cr  $d \to t_{2g}$ + $e_g$
- $\Delta_{trig}: t_{2g} \to a_1 + e_\pi; e_g \to e_\sigma$
- $e_{\pi}$  and  $e_{\sigma}$ :  $\pi$  and  $\sigma$  bonds with S p

half-filled Cr " $t_{2g}$ " states  $\Rightarrow$ no charge or orbital degrees of freedom  $\Rightarrow$ the Heisenberg model should work

### **Spin-spiral calculations**

Magnetization direction is determined by polar angles

- $\theta = const = 0$
- $\phi = \phi_0 + \vec{q} \cdot \vec{R}$

where  $\vec{q}$  is the wave vector of a spin spiral and  $\vec{R}$  is a translation vector If spin-orbit coupling is neglected only off-diagonal in spin terms of the Hamiltonian depend on  $\vec{q}$ :

$$H^{sp} = \left[V_{\uparrow}(r) - V_{\downarrow}(r)\right] \left(\begin{array}{cc} 0 & e^{-i\phi_0} \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} \\ e^{i\phi_0} \sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}} & 0 \end{array}\right)$$

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The Hamiltonian matrix is doubled but remains finite

$$H = \begin{pmatrix} H_{\downarrow \vec{k} - \frac{1}{2}\vec{q}, \downarrow \vec{k} - \frac{1}{2}\vec{q}} & H_{\downarrow \vec{k} - \frac{1}{2}\vec{q}, \uparrow \vec{k} + \frac{1}{2}\vec{q}} \\ H_{\uparrow \vec{k} + \frac{1}{2}\vec{q}, \downarrow \vec{k} - \frac{1}{2}\vec{q}} & H_{\uparrow \vec{k} + \frac{1}{2}\vec{q}, \uparrow \vec{k} + \frac{1}{2}\vec{q}} \end{pmatrix}$$

The total energy  $E(\vec{q})$  can be calculated for an arbitrary single  $\vec{q}$  spin spiral

## **Real-space spin structures**



#### **Real-space spin structures**



the Heisenberg (and the total) energies of the double stripe and  $90^{\circ}$  structures are equal

## **Exchange coupling constants**



 $90^\circ$  vs. DS odd chains:  $JS_0S_{2i+1,j}=0$ 

 $JS_0S_{2i+1,j} + JS_0S_{-2i-1,j} = 0$ 

• S<sub>2</sub> even chains:

 $JS_0S_{2i,j} = JS_0S_{2i,j}$ 

in the HT phase  $J_{nx} = J_{ny} = J_n$ 

$$\varepsilon_{1}(\mathbf{q}) = J_{1} \left[ 2\cos(\sqrt{3}q_{x}a/2)\cos(q_{y}a/2) + \cos(q_{y}a) \right]$$
  

$$\varepsilon_{2}(\mathbf{q}) = J_{2} \left[ \cos(\sqrt{3}q_{x}a) + 2\cos(\sqrt{3}q_{x}a/2)\cos(3q_{y}a/2) \right]$$
  

$$\varepsilon_{3}(\mathbf{q}) = J_{3} \left[ 2\cos(\sqrt{3}q_{x}a)\cos(q_{y}a) + \cos(2q_{y}a) \right]$$

# $E(\vec{q})$ calculated within LSDA



- AFM order along c ( $q_z = \pi/d_c$ ) is preferable
- LiCrS<sub>2</sub>: minimum at  $\vec{q}_{120}$
- AgCrS<sub>2</sub>:  $\vec{q} \approx \vec{q}_{90}$  and  $\vec{q} = \vec{q}_{120}/2$ are almost degenerate
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The tendency Li (120° AFM) $\rightarrow$ Ag (DS) $\rightarrow$ K (FM) is reproduced

## A least-square fit to $J_1$ - $J_3$ , $J_z$ Heisenberg model



M	$J_1$	$J_2$	$J_3$	$J_z$
Li	5.17	0.46	2.73	0.93
Cu	0.16	0.03	1.51	0.82
Ag	-0.14	-0.13	2.45	0.74
Na	-4.06	0.23	2.49	0.09
K	-5.45	0.19	2.11	0.05

- $J_1$  changes sign from AFM to FM
- $J_2$  can be neglected
- $J_3$  is strong and nearly constant
- $J_z$  may be important

## What stabilizes $90^{\circ}$ order in AgCrS<sub>2</sub>



$$z(\mathbf{q}) = J_z \left[ 2\cos\left(\frac{q_z c}{3} - \frac{q_x a}{2\sqrt{3}}\right) \cos\left(\frac{q_y a}{2}\right) + \cos\left(\frac{q_z c}{3} + \frac{q_x a}{\sqrt{3}}\right) \right]$$

Cr layers are displaced  $$\downarrow$$   $J_z$  affects in-plane order



but  $\varepsilon_{III} < \varepsilon_{II}$ 

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90° (DS) order is stabilized by monoclinic distortions

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# Various contributions to the nn superexchange interaction $J_1$



) AFM kinetic exchange due to direct  $t_{2g}$ - $t_{2g}$  hopping

- (b) AFM  $t_{2g}$ -S p- $t_{2g}$  superexchange
- (c) FM  $t_{2g}$ - $t_{2g}$  interaction due to S p Hund's coupling
- (d) FM exchange due to  $t_{2g}$ -S p- $e_g$  hopping
- +  $J_{1a}(d_{CrCr})$ : depends strongly on  $d_{CrCr}$  varies from Li to K
- +  $J_{1b}(d_{\rm CrS})$ : constant AFM contribution as  $d_{\rm CrS}$  does not change
- $J_{1c}(d_{\rm CrS})$ : excluded by test calculations
- +  $J_{1d}(d_{CrS})$ : constant FM contribution;  $|J_{1d}| > |J_{1b}|$

 $J_1$  changes sign due to the competition between AFM  $J_{1a}$  and FM  $J_{1d}(+J_{1b})$ 

# other J's



a plausible path for  $J_3$ : AFM  $t_{2g}\mbox{-}\mbox{S}\ p\mbox{-}\mbox{Cr}\ e_g\mbox{-}\mbox{S}\ p\mbox{-}\ t_{2g}$  superexchange

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- **q** LSDA calculations give "too AFM"  $J_1$  (KCrS<sub>2</sub> is not FM)
- a electronic correlations in Cr d shell are important: in LSDA+U calculations AFM  $J_{1a}$  is suppressed whereas FM  $J_{1d}$  weakly depends on  $U \Rightarrow$  correct magnetic order

#### Conclusions

- Our results allowed us to explain the very interesting sequence of magnetic phases in MCrS<sub>2</sub> compounds, in which the magnetic order in triangular Cr layers changes from purely AFM (120°) in LiCrS<sub>2</sub> via double-stripe structure of AgCrS<sub>2</sub> to FM layers in KCrS<sub>2</sub>
- These magnetic structures appear because of competing the nearest neighbor exchange interaction  $J_1$ , which changes sign from AFM to FM as  $d_{\rm CrCr}$  increases, and AFM third-neighbor  $J_3$
- In turn, the strength of  $J_1$  is determined by the competition of two contributions of opposite signs:
  - $\circ$  AFM Cr  $t_{2g}$ -Cr  $t_{2g}$  exchange
  - $\circ~$  FM exchange between half-filled Cr  $t_{2g}$  and empty Cr  $e_g$  states via S p states

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Open question:

Multiferroic properties of AgCrS $_2$