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Azurite: a highly frustrated quasi-1D antiferromagnet

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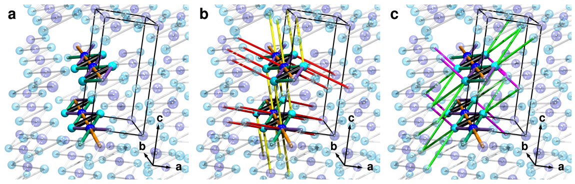
Motivation

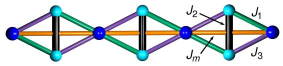
- **Azurite:** known as precious stone & pigment since ancient times
- plateau at 1/3 of saturation magnetization in low-temperature magnetization curve [1, 2]
- distorted diamond chain (?) [1]
- microscopic model controversial [1, 3–8]:
  - frustrated magnet ?
  - dimensionality ?

Arrangement of Cu^{2+} ions in the structure of azurite



J_1, J_2, J_3, J_m — J_5, J_6 — J_4, J_7

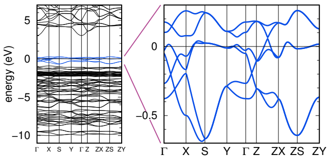
Generalized diamond chain model



Spin-1/2 Heisenberg Hamiltonian:

$$\mathcal{H} = \sum_{\langle i,j\rangle} J_{i,j}\,\vec{S}_i\cdot\vec{S}_j - H\sum_i S_i^z$$

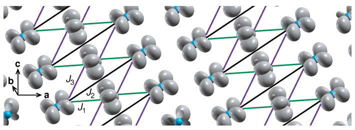
DFT: band structure



- copper $d_{x^2-y^2}$ bands at Fermi level (metal)
- tight-binding fit (NMTO downfoldig) $\Rightarrow t_i$
- idenfication of relevant antiferromagnetic $J_i \propto t_i^2/U$

DFT: electron density

charge density isosurface for $E \geq -0.75$meV



$\Rightarrow$ $d_{x^2-y^2}$-character of relevant copper orbitals

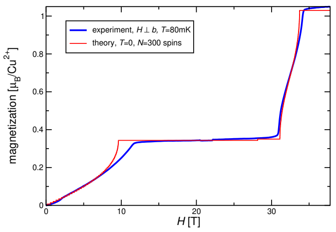
at variance with x-ray scattering [9]

GGA+$U = 8$eV: J_i [K]

	J_1	J_2	J_3	J_4	J_5	J_6	J_7	J_m	J_d
full	13.5	42.8	12.5	2.7	0.6	4.4	−1.7	2.6	−0.4
minimal	17.9	43.9	12.0	–	–	–	–	2.4	–
refined	15.51	33	6.93	–	–	–	–	4.62	–
Ref. [1]	19	24	8.6	–	–	–	–	–	–

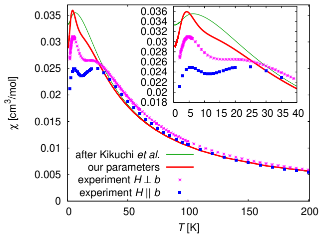
- J_2 dominant
- $J_4 - J_7$: contribute only in higher order perturbation theory
  - $\Rightarrow$ irrelevant for low-energy behavior
  - $\Rightarrow$ effective generalized diamond chain (including J_m)

Magnetization curve



- Comparison with [2] sets energy scale: $J_2 = 33$K

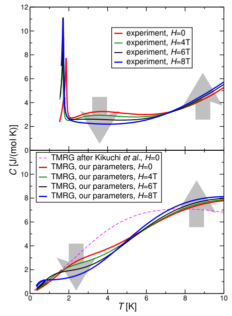
Magnetic susceptibility



- our values for J: double-„peak" structure at correct temperatures ✔
  – in contrast to single peak for original values for J [1]

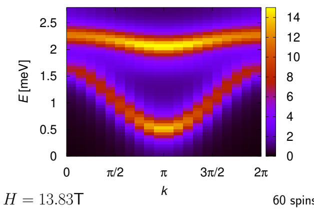
Specific heat

- $H = 0$: peak at $T \approx 3 \ldots 4$K ✔
  – absent for original J-values [1] (compare [4])
- low-T peak suppressed with increasing H ✔
- $7\text{K} \leq T \leq 10\text{K}$: specific heat C increases with increasing T and H ✔
- experiment: ordering peak at $T \approx 2$K
  $\Rightarrow$ interchain coupling



Inelastic neutrons at $M = 1/3$

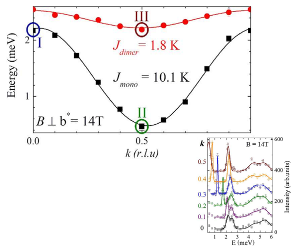
Transverse dynamic structure factor



$H = 13.83$T

60 spins
open boundary conditions

Experiment [5]

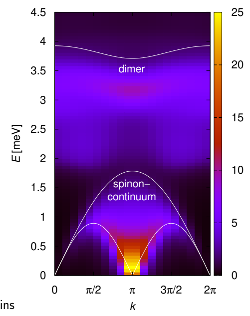


$$S^{xx}(\vec{k},\omega) = \frac{3}{N}\sum_{\langle x,y\rangle} e^{i\vec{k}\cdot(\vec{R}_x-\vec{R}_y)}\,\mathrm{Im}\langle 0|S_x^x\frac{1}{\omega+E_0-\mathcal{H}+i\eta}S_y^x|0\rangle$$

Good agreement ✔

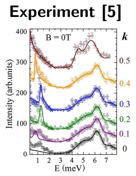
Inelastic neutrons at $H = 0$

Dynamic structure factor [10]



60 spins
open boundary conditions

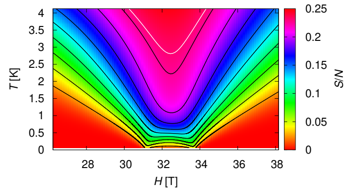
Experiment [5]



- semi-quantitative agreement between theory and experiment ✔
- „dimer" excitation: shifted, renormalized, and broadened from $M = 1/3 \to 0$
- „monomer" excitation with J_{eff}:
  - sharp at $M = 1/3$
  - two-spinon continuum at $M = 0$

Magnetocaloric effect [10]

expected isentropes and entropy in the high-field regime



- quasi-degeneracy with entropy $S/N = (\ln 2)/3$ (white line) split
- cooling by adiabatic (de)-magnetization from $T \approx 1.4\text{K} \to\approx 100\text{mK}$ expected

Summary

- generalized diamond chain model derived by first-principles computations as an effective model for azurite [14]: explains a broad range of experiments [1, 2, 5] (including NMR [11] – not shown) ✔
- 3D coupling geometry computed: zero-field [12] and high-field order [13] remain to be analyzed
- enhanced magnetocaloric effect predicted in the high-field regime of azurite [10]

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