Neessity of RVB States in Solid State Quantum Chemistry.

Lesson of CuNCN.

A.L. Tchougréeff

[1] Institut für Anorganische Chemie
RWTH - Aachen University

[2] Poncelet Lab,
Independent University of Moscow

RCTF2014 02.07.2014

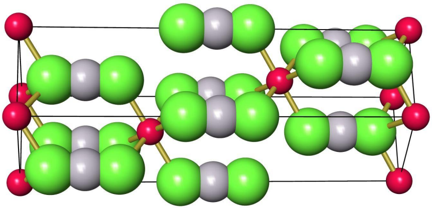
Outline

Outline

1. CuNCN case study
2. Lessons.

Outline

Physical properties.
Structure.



Formula:	$Cr_2(NCN)_3$	MnNCN	FeNCN	CoNCN	NiNCN	CuNCN
Color:	green	green	dark-red	orange-brown	light-brown	black
T_c (K)	**175**	28	345	255	360	?

Outline

CuNCN - an isolated case.

Structure.

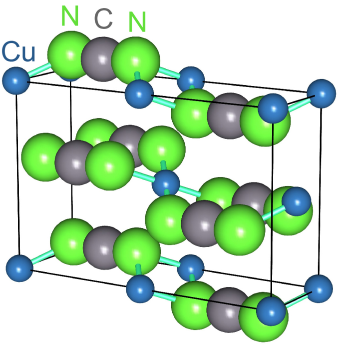


Figure: Structure CuNCN.

CuNCN - an isolated case.

Physical properties.

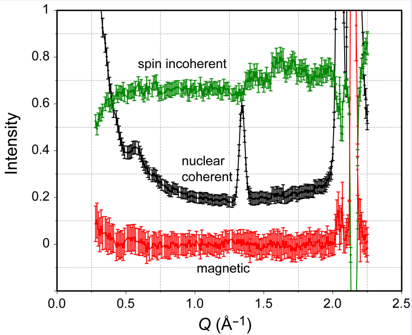
Absence of magnetic structure.

Susceptibility: Pauli vs. Arrhenius

CuNCN - an isolated case.

Physical properties.

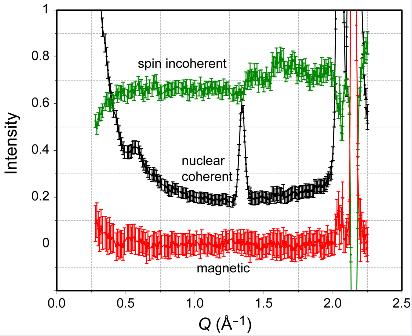
Absence of magnetic structure.



Susceptibility: Pauli vs. Arrhenius

CuNCN - an isolated case.
Physical properties.

Absence of magnetic structure.

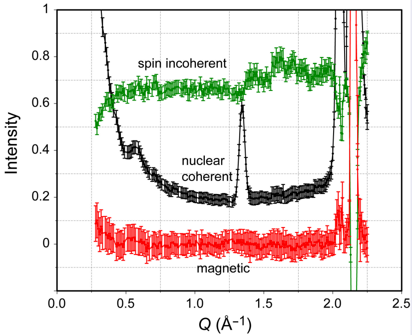


Susceptibility: Pauli vs. Arrhenius

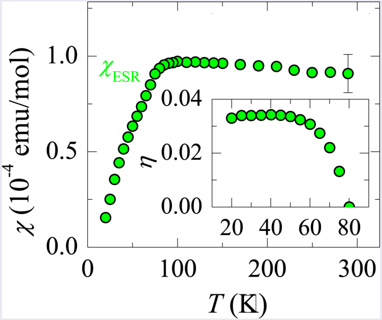
CuNCN - an isolated case.

Physical properties.

Absence of magnetic structure.

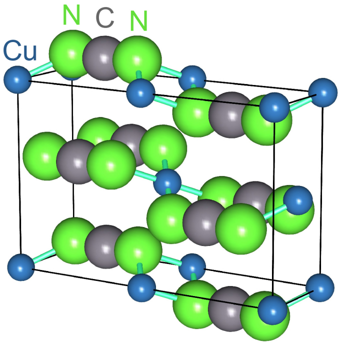


Susceptibility: Pauli vs. Arrhenius

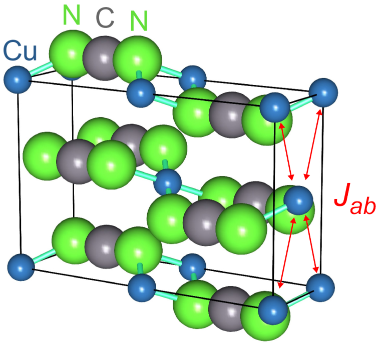


Attempt to understand.

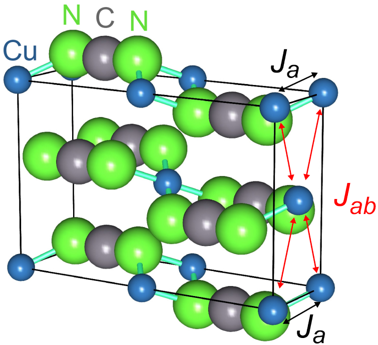
"Triangular" model



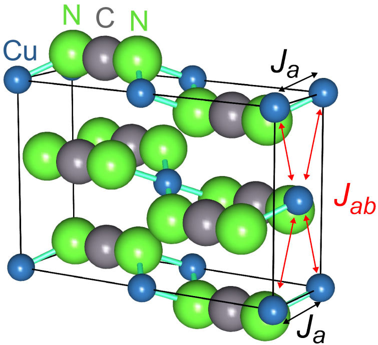
Attempt to understand.
"Triangular" model

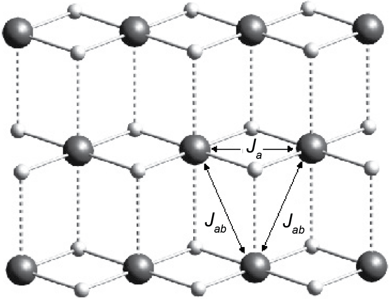


Attempt to understand.
"Triangular" model



Attempt to understand.
"Triangular" model

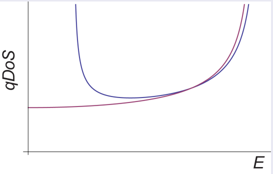




"Triangular" model explained the CuNCN physics by 1D- to 2D-RVB transition in the *ab* plane accompanied by opening the gap:

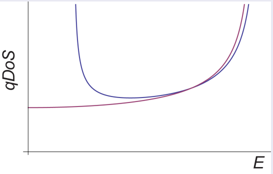
however, structure data show anomalies in *a* and in *c* lattice constants, although not in *b*.

"Triangular" model explained the CuNCN physics by 1D- to 2D-RVB transition in the *ab* plane accompanied by opening the gap:



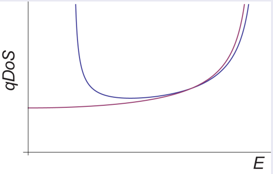
however, structure data show anomalies in *a* and in *c* lattice constants, although not in *b*.

"Triangular" model explained the CuNCN physics by 1D- to 2D-RVB transition in the *ab* plane accompanied by opening the gap:

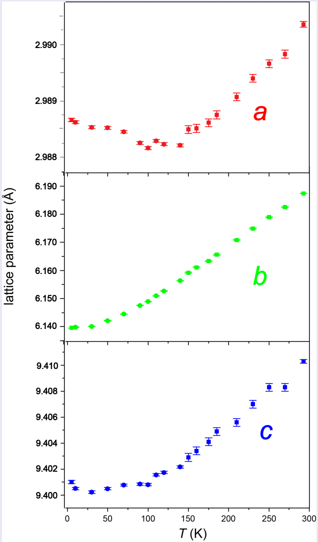


however, structure data show anomalies in *a* and in *c* lattice constants, although not in *b*.

"Triangular" model explained the CuNCN physics by 1D- to 2D-RVB transition in the *ab* plane accompanied by opening the gap:

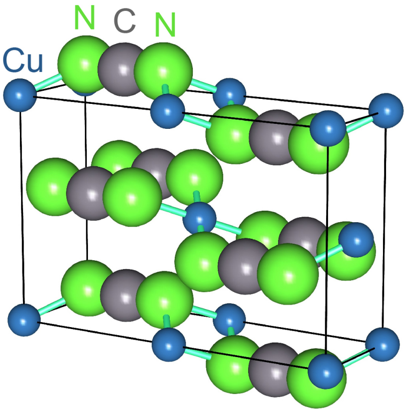


however, structure data show anomalies in *a* and in *c* lattice constants, although not in *b*.



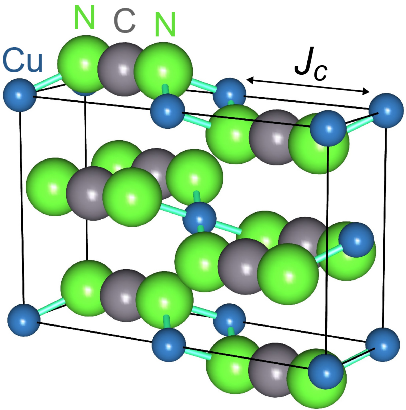
RVB States of c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



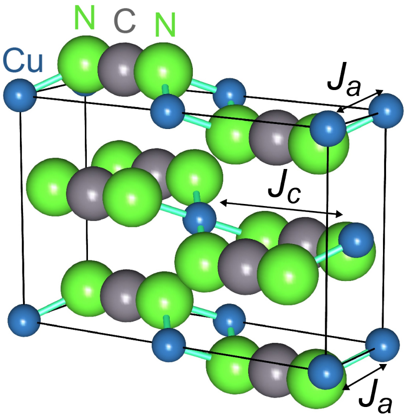
RVB States of c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



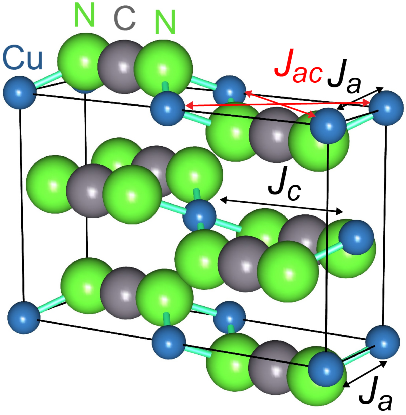
RVB States of c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



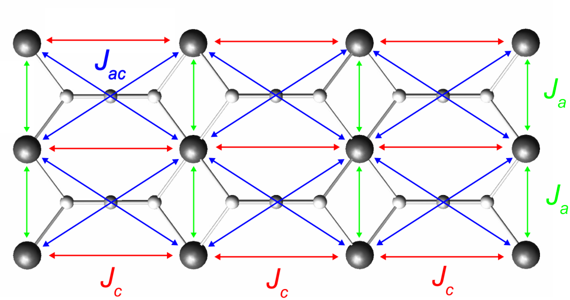
RVB States of c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



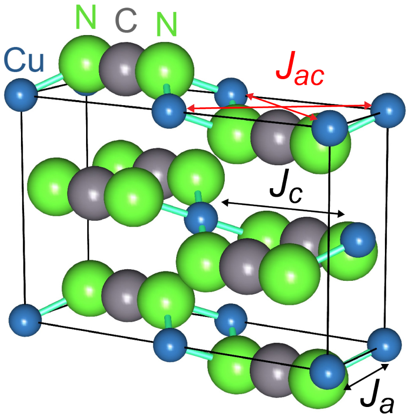
c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



Heisenberg Hamiltonian

$$\sum_{\mathbf{r}}\sum_{\tau} J_{\tau}\mathbf{S}_{\mathbf{r}}\mathbf{S}_{\mathbf{r}+\tau} \quad (1)$$

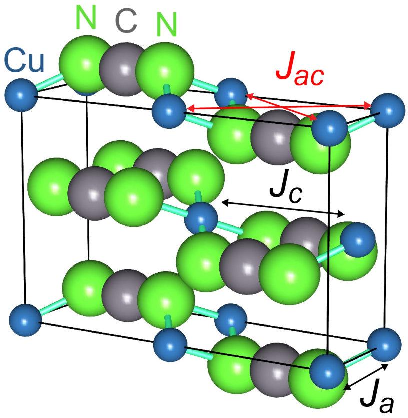
$$\mathbf{S}_{\mathbf{r}} = \frac{1}{2} c^{+}_{\mathbf{r}\alpha}\sigma_{\alpha\beta}c_{\mathbf{r}\beta}, \quad (2)$$

RVB order parameters

$$\begin{aligned} \xi_{\tau} &= \left\langle c^{+}_{\mathbf{r}+\tau\sigma}c_{\mathbf{r}\sigma}\right\rangle \\ \Delta_{\tau} &= \left\langle c_{\mathbf{r}\alpha}c_{\mathbf{r}+\tau\beta}\right\rangle \end{aligned} \quad (3)$$

c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



Heisenberg Hamiltonian

$$\sum_{\mathbf{r}}\sum_{\tau} J_{\tau}\mathbf{S}_{\mathbf{r}}\mathbf{S}_{\mathbf{r}+\tau} \quad (1)$$

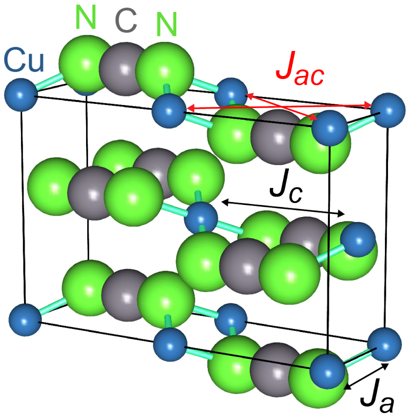
$$\mathbf{S}_{\mathbf{r}} = \frac{1}{2} c^{+}_{\mathbf{r}\alpha}\sigma_{\alpha\beta}c_{\mathbf{r}\beta}, \quad (2)$$

RVB order parameters

$$\xi_{\tau} = \left\langle c^{+}_{\mathbf{r}+\tau\sigma}c_{\mathbf{r}\sigma}\right\rangle$$
$$\Delta_{\tau} = \left\langle c_{\mathbf{r}\alpha}c_{\mathbf{r}+\tau\beta}\right\rangle \quad (3)$$

c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



Heisenberg Hamiltonian

$$\sum_{\mathbf{r}}\sum_{\tau} J_\tau \mathbf{S}_\mathbf{r}\mathbf{S}_{\mathbf{r}+\tau} \quad (1)$$

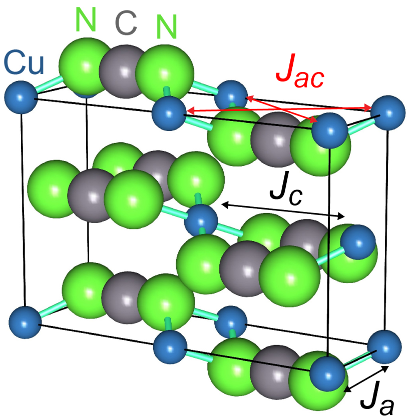
$$\mathbf{S}_\mathbf{r} = \frac{1}{2} c^+_{\mathbf{r}\alpha}\sigma_{\alpha\beta}c_{\mathbf{r}\beta}, \quad (2)$$

RVB order parameters

$$\xi_\tau = \langle c^+_{\mathbf{r}+\tau\sigma}c_{\mathbf{r}\sigma}\rangle$$
$$\Delta_\tau = \langle c_{\mathbf{r}\alpha}c_{\mathbf{r}+\tau\beta}\rangle \quad (3)$$

c-a-ca Heisenberg antiferromagnet.

Another option for frustration.



Heisenberg Hamiltonian

$$\sum_{\mathbf{r}}\sum_{\tau} J_\tau \mathbf{S}_{\mathbf{r}} \mathbf{S}_{\mathbf{r}+\tau} \quad (1)$$

$$\mathbf{S}_{\mathbf{r}} = \frac{1}{2} c^{+}_{\mathbf{r}\alpha} \sigma_{\alpha\beta} c_{\mathbf{r}\beta}, \quad (2)$$

RVB order parameters

$$\xi_\tau = \left\langle c^{+}_{\mathbf{r}+\tau\sigma} c_{\mathbf{r}\sigma} \right\rangle$$
$$\Delta_\tau = \left\langle c_{\mathbf{r}\alpha} c_{\mathbf{r}+\tau\beta} \right\rangle \quad (3)$$

RVB treatment.

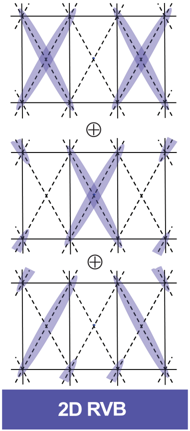
Mean-field RVB: Dispersion

$$
\begin{aligned}
E_{\mathbf{k}} &= \sqrt{\xi_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2}; \\
E_{\mathbf{k}}^2 &= 9\left(J_a^2\zeta_a^2\cos^2\mathbf{k}_a + J_c^2\zeta_c^2\cos^2\mathbf{k}_c + 4J_{ac}^2\zeta_{ac}^2\cos^2\mathbf{k}_a\cos^2\mathbf{k}_c\right), \\
\zeta_\tau^2 &= \xi_\tau^2 + \eta_\tau^2,\ \Delta_\tau = \eta_\tau e^{i\phi_\tau}
\end{aligned}
$$

Free energy

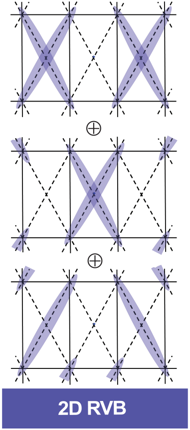
$$
\begin{aligned}
F &= 3J_a\zeta_a^2 + 3J_c\zeta_c^2 + 6J_{ac}\zeta_{ac}^2 - \frac{2\theta}{4\pi^2}\int_{BZ} \ln\left(2\cosh\left(\frac{E_{\mathbf{k}}}{2\theta}\right)\right) d^2\mathbf{k} \\
&= 3J_a\zeta_a^2 + 3J_c\zeta_c^2 + 6J_{ac}\zeta_{ac}^2 - 2\theta\int \ln\left(2\cosh\left(\frac{\varepsilon}{2\theta}\right)\right) g(\varepsilon)d\varepsilon
\end{aligned}
$$

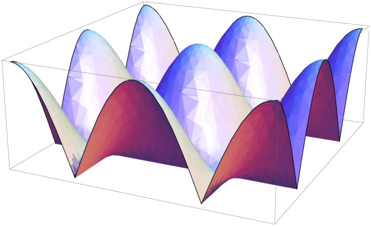
gapless 2D-RVB



$$\zeta_a, \zeta_c = 0; \zeta_{ac} \neq 0$$

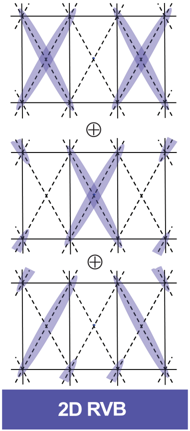
gapless 2D-RVB

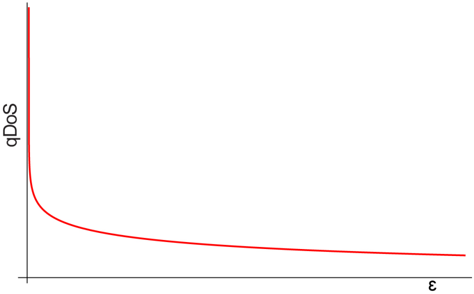




$\zeta_a, \zeta_c = 0; \zeta_{ac} \neq 0$

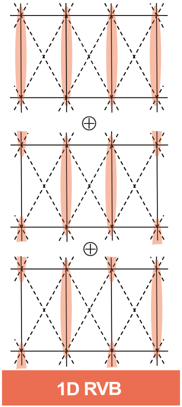
gapless 2D-RVB





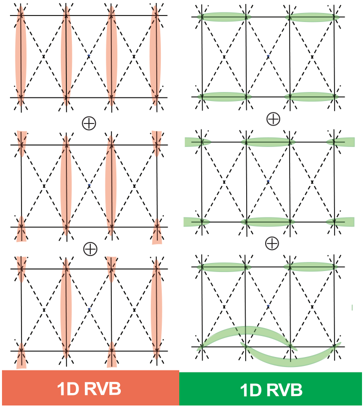
$\zeta_a, \zeta_c = 0; \zeta_{ac} \neq 0$

1D-RVB



$$\zeta_c \neq 0; \zeta_a, \zeta_{ac} = 0$$

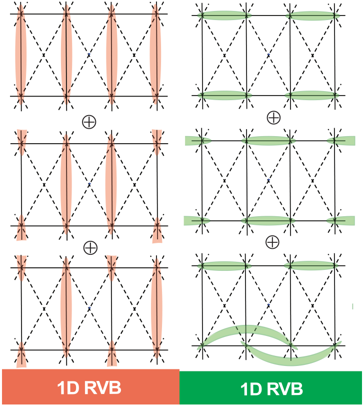
1D-RVB

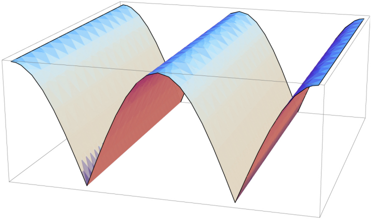


$\zeta_c \neq 0;\ \zeta_a, \zeta_{ac} = 0$

$\zeta_a \neq 0;\ \zeta_c, \zeta_{ac} = 0$

1D-RVB

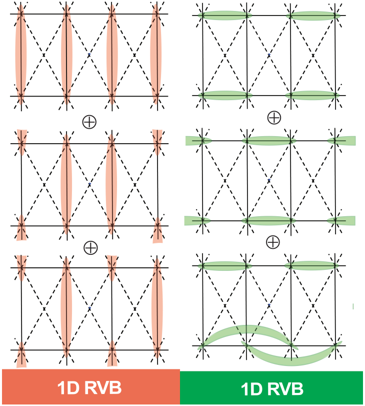


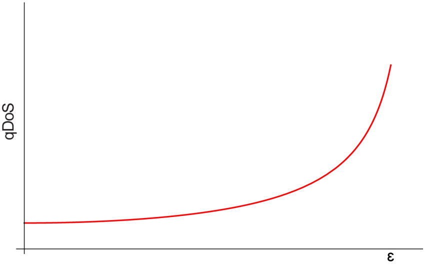


$\zeta_c \neq 0;\ \zeta_a, \zeta_{ac} = 0$

$\zeta_a \neq 0;\ \zeta_c, \zeta_{ac} = 0$

1D-RVB

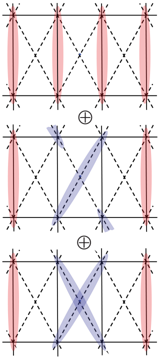




$\zeta_c \neq 0; \zeta_a, \zeta_{ac} = 0$

$\zeta_a \neq 0; \zeta_c, \zeta_{ac} = 0$

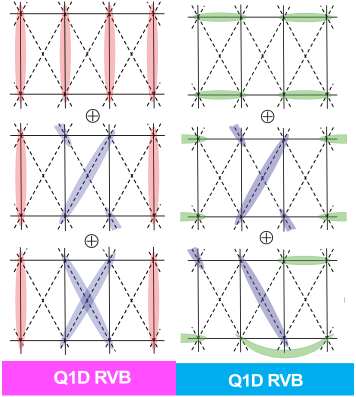
Q1D-RVB



Q1D RVB

$$\zeta_c, \zeta_{ac} \neq 0; \ \zeta_a = 0$$

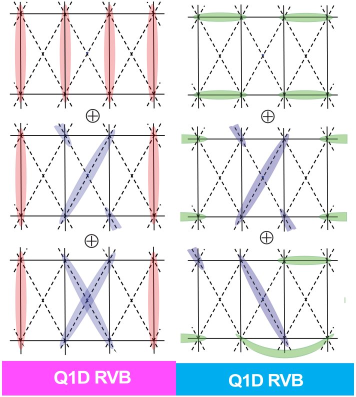
Q1D-RVB

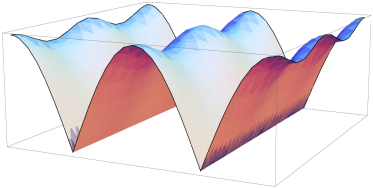


$\zeta_c, \zeta_{ac} \neq 0; \zeta_a = 0$

$\zeta_a, \zeta_{ac} \neq 0; \zeta_c = 0$

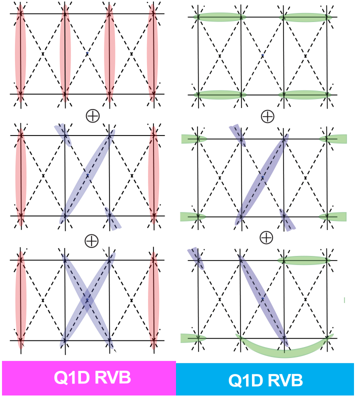
Q1D-RVB

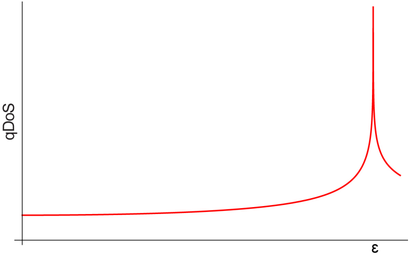




$$\zeta_c, \zeta_{ac} \neq 0;\ \zeta_a = 0$$
$$\zeta_a, \zeta_{ac} \neq 0;\ \zeta_c = 0$$

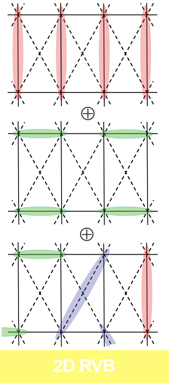
Q1D-RVB





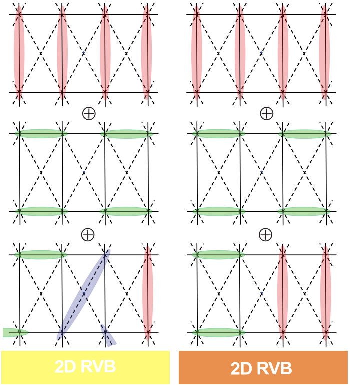
$$\zeta_c, \zeta_{ac} \neq 0; \ \zeta_a = 0$$
$$\zeta_a, \zeta_{ac} \neq 0; \ \zeta_c = 0$$

2D-RVB



$\zeta_c, \zeta_a, \zeta_{ac} \neq 0$

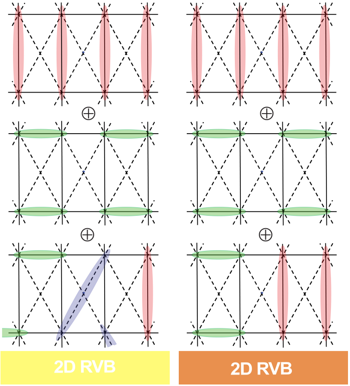
2D-RVB

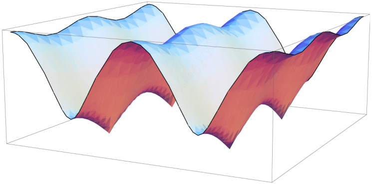


$$\zeta_c, \zeta_a, \zeta_{ac} \neq 0$$

$$\zeta_c, \zeta_a \neq 0; \zeta_{ac} = 0$$

2D-RVB

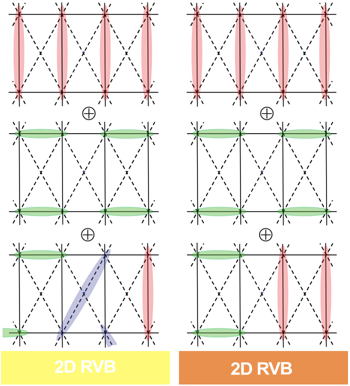


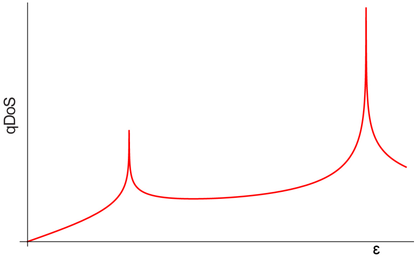


$\zeta_c, \zeta_a, \zeta_{ac} \neq 0$

$\zeta_c, \zeta_a \neq 0; \zeta_{ac} = 0$

2D-RVB



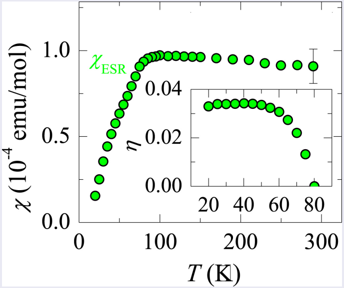


$\zeta_c, \zeta_a, \zeta_{ac} \neq 0$

$\zeta_c, \zeta_a \neq 0; \zeta_{ac} = 0$

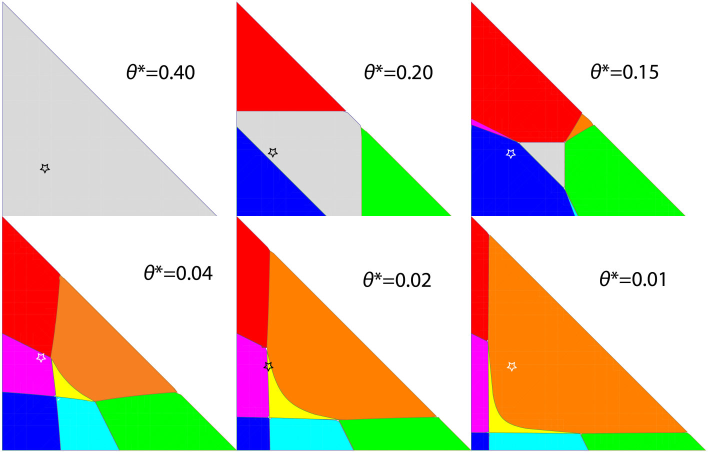
Magnetic Properties
ESR data.

Material characterisitcs from fit of experimental data.



EPR experiment on the left is reproduced with the parameters:
$J_c = 1310$ K, $J_{ac} = 1400$ K,
$J_a = 560$ K;
$\theta^{crit}_{ac} = 535$ K; $\theta^{crit}_{c,ac} = 435$ K;
$\theta^{crit}_{c,ac \to c,a,ac} = 100$ K,

Phase diagram.
High-temperature limit.



With temperature θ^* as a fraction of $J_a^* + J_c^* + J_{ac}^* = 1$.

Nessessary spare parts.

Supplying the total energy by the structure dependent terms:

Elastic energy

$$\frac{1}{2}\sum_{\mu\lambda} K_{\mu\lambda}\rho_{\mu}\rho_{\lambda} \quad (4)$$

Magnetostriction

$$J_{\tau} = J_{\tau 0} + \sum_{\lambda} J'_{\tau,\lambda}\rho_{\lambda}. \quad (5)$$

And using:

Mechanical equilibrium condition

$$\frac{\partial F}{\partial \rho_{\lambda}} + \sum_{\mu\lambda} K_{\mu\lambda}\rho_{\mu} = 0. \quad (6)$$

Nessessary spare parts.

Supplying the total energy by the structure dependent terms:

Elastic energy

$$\frac{1}{2}\sum_{\mu\lambda} K_{\mu\lambda}\rho_{\mu}\rho_{\lambda} \tag{4}$$

Magnetostriction

$$J_{\tau} = J_{\tau 0} + \sum_{\lambda} J'_{\tau,\lambda}\rho_{\lambda}. \tag{5}$$

And using:

Mechanical equilibrium condition

$$\frac{\partial F}{\partial \rho_{\lambda}} + \sum_{\mu\lambda} K_{\mu\lambda}\rho_{\mu} = 0. \tag{6}$$

Geometry of RVB states.

We obtain

Equilibrium geometry in an RVB phase:

$$\rho_\mu = \sum_\lambda (K)^{-1}_{\mu\lambda} \left(\sum_\tau A_\tau \zeta_\tau^2 J'_{\tau,\lambda} \right). \quad (7)$$

After "some algebra" we conclude that the

Temperature dependence of geometry

is that of squared pseudogaps: $A = 3J_a\zeta_a$ and $C = 3J_c\zeta_c$:

$$\begin{pmatrix} \delta a \\ \delta c \end{pmatrix} = \alpha T \begin{pmatrix} a \\ c \end{pmatrix} + \begin{pmatrix} \Lambda_{A,a} \\ \Lambda_{A,c} \end{pmatrix} A^2 + \begin{pmatrix} \Lambda_{C,a} \\ \Lambda_{C,c} \end{pmatrix} C^2 \quad (8)$$

where Λ's are combinations of exchange, elastic, and magnetostriction parameters.

Geometry of RVB states.

We obtain

Equilibrium geometry in an RVB phase:

$$\rho_\mu = \sum_\lambda (K)^{-1}_{\mu\lambda} \left(\sum_\tau A_\tau \zeta_\tau^2 J'_{\tau,\lambda} \right). \qquad (7)$$

After "some algebra" we conclude that the

Temperature dependence of geometry

is that of squared pseudogaps: $A = 3J_a\zeta_a$ and $C = 3J_c\zeta_c$:

$$\begin{pmatrix} \delta a \\ \delta c \end{pmatrix} = \alpha T \begin{pmatrix} a \\ c \end{pmatrix} + \begin{pmatrix} \Lambda_{A,a} \\ \Lambda_{A,c} \end{pmatrix} A^2 + \begin{pmatrix} \Lambda_{C,a} \\ \Lambda_{C,c} \end{pmatrix} C^2 \qquad (8)$$

where Λ's are combinations of exchange, elastic, and magnetostriction parameters.

Structure manifestations of RVB transitions

a and c anomalies at 100 K: $ac, c \rightarrow ac, c, a$

Assuming the C pseudogap to access its limiting value and not changing any more

$$\begin{pmatrix} \Lambda_{A,a} \\ \Lambda_{A,c} \end{pmatrix} = \frac{J'_{a,a}}{3J_a^2 \left|K\right|} \begin{pmatrix} K_{cc} \\ -K_{ac} \end{pmatrix} \tag{9}$$

Structure manifestations of RVB transitions

a and c anomalies at 30 K: $ac, c, a \rightarrow c, a$

$$\frac{d}{d\theta}\begin{pmatrix}\delta a\\ \delta c\end{pmatrix}\Bigg|_{\theta\rightarrow\theta^{\mathrm{crit}}} = -\frac{1}{\theta^{\mathrm{crit}}}C^{*2}\begin{pmatrix}\Lambda_{C,a}\\ \Lambda_{C,c}\end{pmatrix} \quad (10)$$

Structure manifestations of RVB transitions

a and c anomalies at 30 K: $ac, c, a \rightarrow c, a$

$$\frac{d}{d\theta}\begin{pmatrix}\delta a\\ \delta c\end{pmatrix}\Bigg|_{\theta\rightarrow\theta^{\mathrm{crit}}} = -\frac{1}{\theta^{\mathrm{crit}}}C^{*2}\begin{pmatrix}\Lambda_{C,a}\\ \Lambda_{C,c}\end{pmatrix} \quad (10)$$

Structure manifestations of RVB transitions

a and c anomalies at 30 K: $ac, c, a \rightarrow c, a$

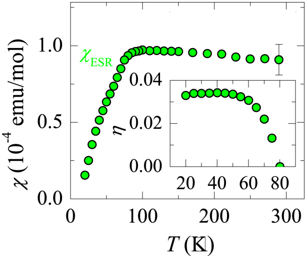
$$\frac{d}{d\theta}\left(\begin{array}{c}\delta a\\ \delta c\end{array}\right)\Bigg|_{\theta\rightarrow\theta^{\mathrm{crit}}} = -\frac{1}{\theta^{\mathrm{crit}}}C^{*2}\left(\begin{array}{c}\Lambda_{C,a}\\ \Lambda_{C,c}\end{array}\right) \quad (10)$$

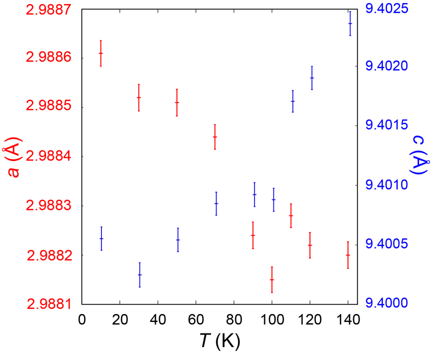
$$\begin{array}{ccccc} \mathrm{Q1D-RVB} & \rightarrow & \mathrm{2D-RVB} & \rightarrow & \mathrm{2D-RVB} \\ \zeta_c, \zeta_{ac} & \rightarrow & \zeta_c, \zeta_{ac}, \zeta_a & \rightarrow & \zeta_c, \zeta_a \\ \theta^{\mathrm{crit}} > 0 & & \theta^{\mathrm{crit}} > 0 & & \theta^{\mathrm{crit}} < 0 \\ \frac{3J_{ac}J_c}{8(3J_{ac}-2J_c)} & & \frac{3J_{ac}J_c}{8(3J_{ac}-2J_c)} & & \frac{3J_aJ_c}{8(3J_a-2J_c)} \end{array} \quad (11)$$

Outline

Structure effect of 1D to 2D RVB-transition on CuNCN.

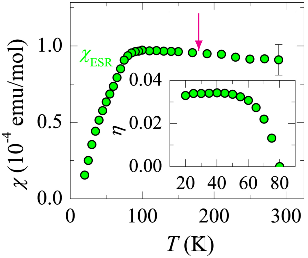
What one can expect?



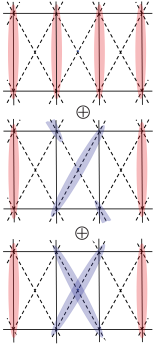


Structure effect of 1D to 2D RVB-transition on CuNCN.

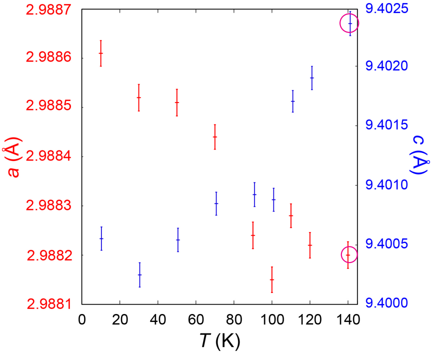
What one can expect?



$\zeta_c, \zeta_{ac} > 0, \zeta_a = 0$

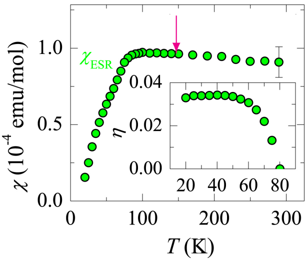


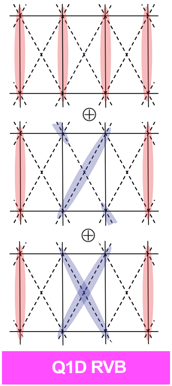
Q1D RVB

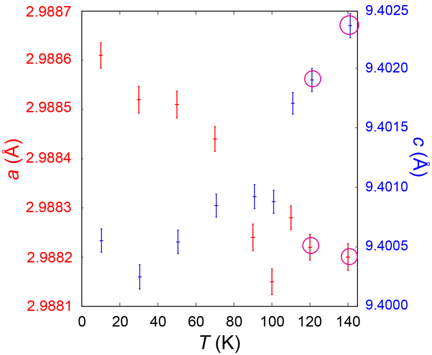


Structure effect of 1D to 2D RVB-transition on CuNCN.

What one can expect?



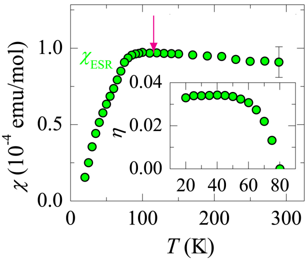




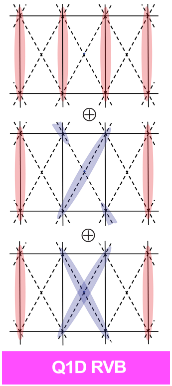
$\zeta_c, \zeta_{ac} > 0, \zeta_a = 0$

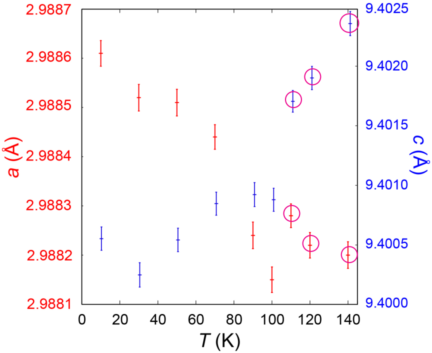
Structure effect of 1D to 2D RVB-transition on CuNCN.

What one can expect?



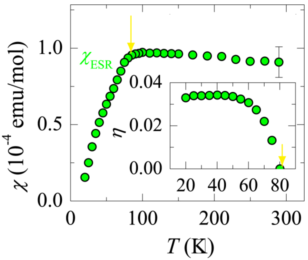
$\zeta_c, \zeta_{ac} > 0, \zeta_a = 0$



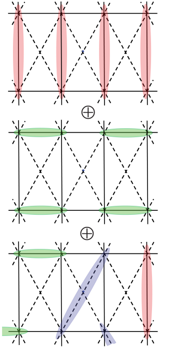


Structure effect of 1D to 2D RVB-transition on CuNCN.

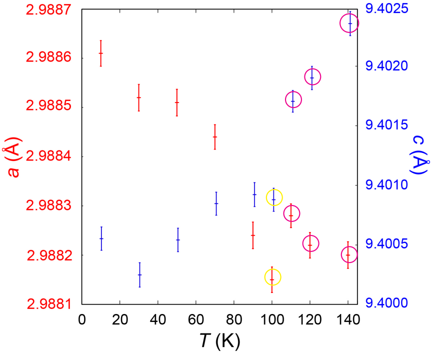
What one can expect?



$\zeta_c, \zeta_{ac}, \zeta_a > 0$

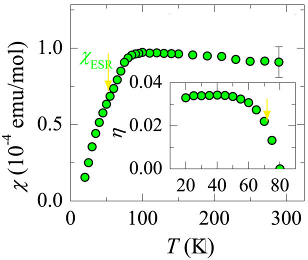


2D RVB

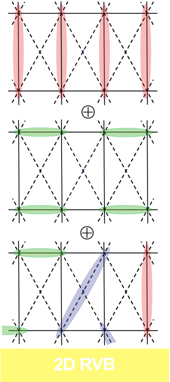


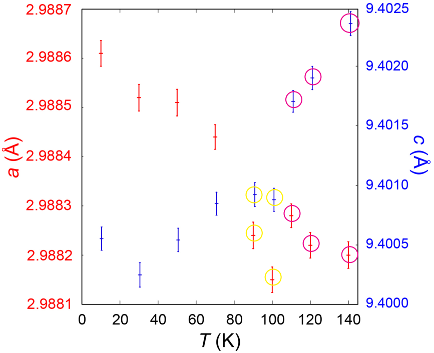
Structure effect of 1D to 2D RVB-transition on CuNCN.

What one can expect?



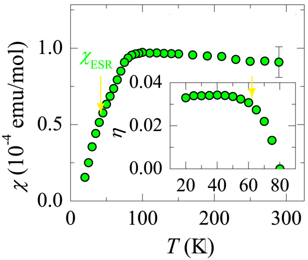
$\zeta_c, \zeta_{ac}, \zeta_a > 0$



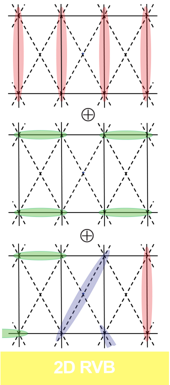


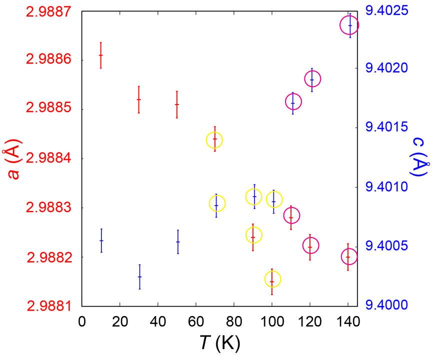
Structure effect of 1D to 2D RVB-transition on CuNCN.

What one can expect?



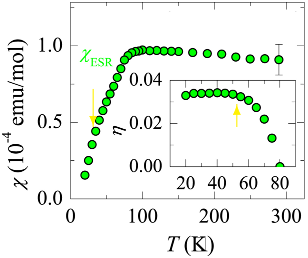
$\zeta_c, \zeta_{ac}, \zeta_a > 0$



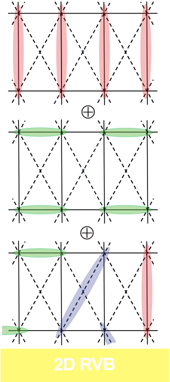


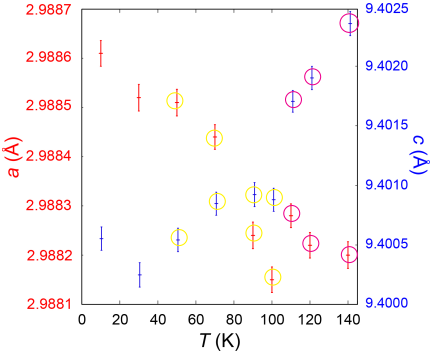
Structure effect of 1D to 2D RVB-transition on CuNCN.

What one can expect?



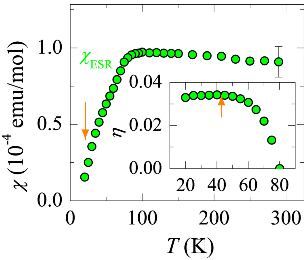
$\zeta_c, \zeta_{ac}, \zeta_a > 0$



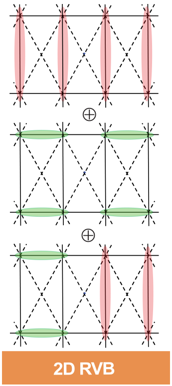


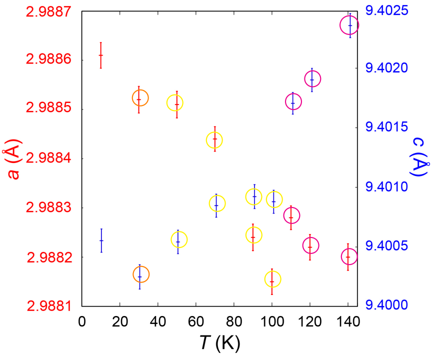
Structure effect of 1D to 2D RVB-transition on CuNCN.

What one can expect?



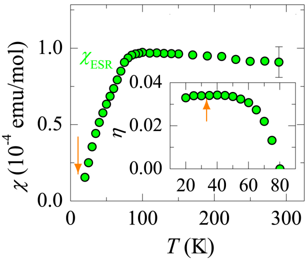
$$\zeta_c, \zeta_{ac}, \zeta_a > 0$$



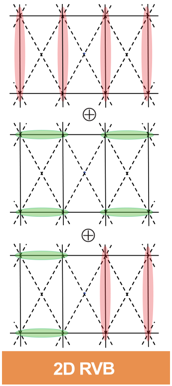


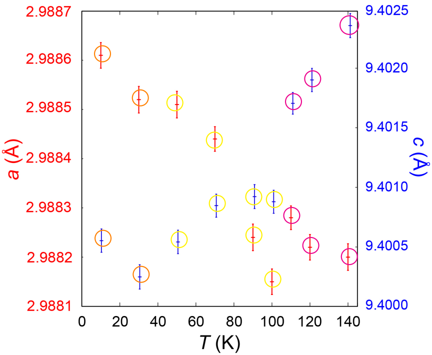
Structure effect of 1D to 2D RVB-transition on CuNCN.

What one can expect?



$\zeta_c, \zeta_a > 0, \zeta_{ac} = 0$

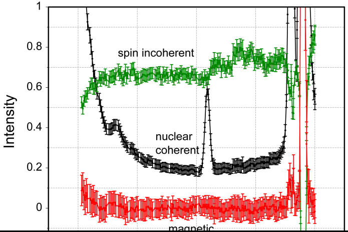




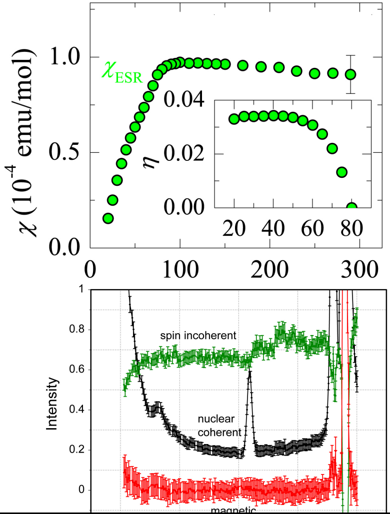
Outline

Conclusions *dictum* Synthesis

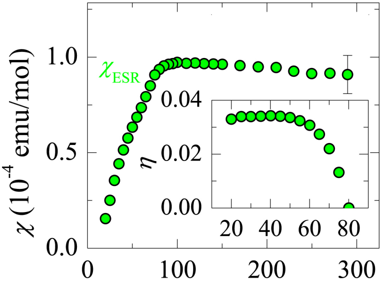
Conclusions *dictum* Synthesis

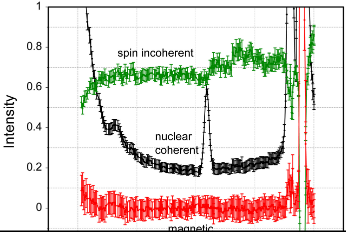


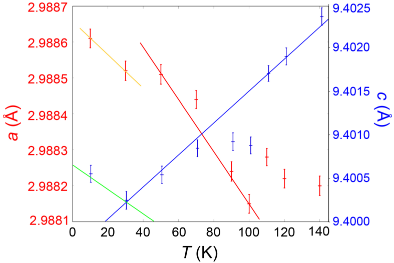
Conclusions *dictum* Synthesis



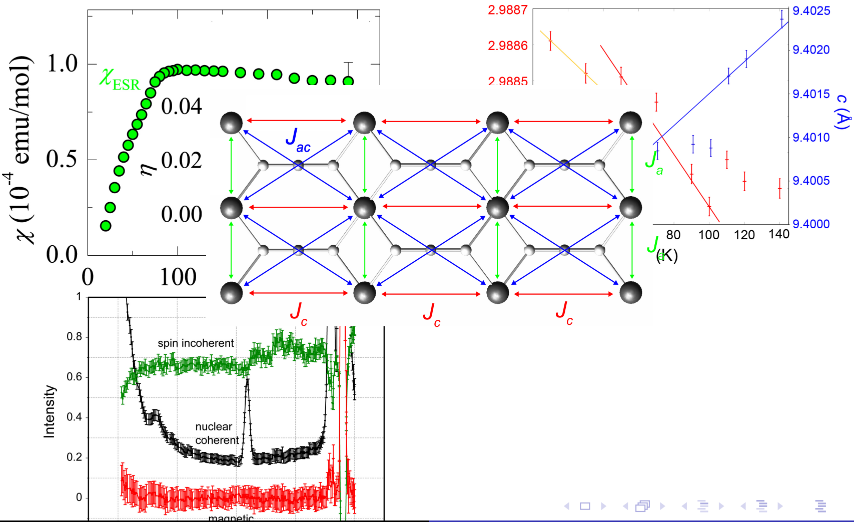
Conclusions *dictum* Synthesis



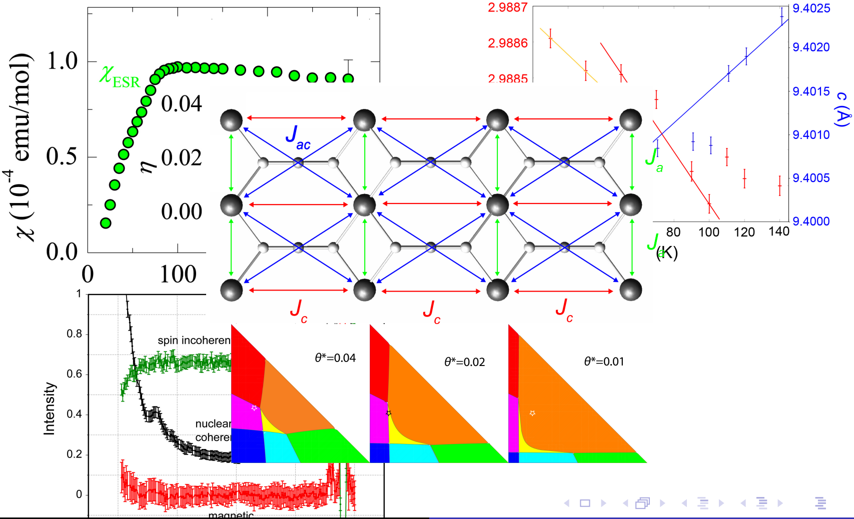




Conclusions *dictum* Synthesis



Conclusions *dictum* Synthesis



Outline

Lessons.

- No available solid state quantum chemistry package produces any RVB solution: no Δ's are available.
- No available solid state quantum chemistry package produces temperature dependent electronic state.

Lessons.

- No available solid state quantum chemistry package produces any RVB solution: no Δ's are available.
- No available solid state quantum chemistry package produces temperature dependent electronic state.

Acknowledgments

SNBL ESRF

Dr. Wouter van Beek

University of Cologne

Prof. Dr. Uwe Ruschewitz

Jožef Stefan Institute, Ljubljana

Dr. A. Zorko, Dr. P. Jeglič, Dr. A. Potočnik, Prof. Dr. D. Arčon

Funding

DFG