Ring Exchanges in Solid $^3$He

by

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Introduction to solid $^3$He
Direct exchange interactions
Nuclear spin orderings
Ring exchange model
First principles calculations of ring exchanges
Quantitative comparison between recent experiments and the calculations
Future prospects and brief introductions to other systems
Interactions in He systems

**He systems**

Lennard-Jones potential:

\[ U_{\text{L-J}}(r) = 4\varepsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right\} \]

- strong short-range repulsion (hardcore)
- weak long-range attraction (van der Waals)

Kinetic energy:

\[ K(r) = \frac{\hbar^2}{2mr^2} \]

- large zero-point energy

stronger correlations at **higher** densities

**Electron systems**

Coulomb potential:

\[ U_{\text{coulomb}}(r) = \left( \frac{1}{4\pi\varepsilon_0} \right) \frac{e^2}{r} \]

- long-range repulsion

stronger correlations at **lower** densities
Liquid and solid $^3$He

- $^3$He: composite fermion
- nuclear spin ($S = 1/2$)
- isotropic ($^1S$ closed shell)
- no impurities (superclean!)
- large zero-point motion
- highly correlated
- highly tunable

Quantum liquid and solid
Low temperature phase diagram of $^3$He

Liquid phase
- correlated Fermi liquid
  - almost localized or nearly ferromagnetic
- spin triplet p-wave BCS states

Until this age, at least in textbook, nuclear magnetism of solid $^3$He had been known as a typical example of paramagnetism.

Pomeranchuk (1950) prediction of $T_c \approx 0.1 \text{ } \mu \text{K}$
dipole-dipole interactions ($E_{d-d}$)

Bernades-Primakoff (1960) prediction of $T_c \approx 100 \text{ } \text{mK}$
direct exchange interactions ($J$)
Heisenberg Model: effective spin Hamiltonian

Total wave function ($\Psi$) of two fermions:

\[
\Psi_{\text{singlet}}(r_1, r_2) = \frac{1}{\sqrt{2}} \left\{ \phi_i(r_1)\phi_j(r_2) + \phi_i(r_2)\phi_j(r_1) \right\} \frac{1}{\sqrt{2}} \left\{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \right\}
\]

\[
\Psi_{\text{triplet}}(r_1, r_2) = \frac{1}{\sqrt{2}} \left\{ \phi_i(r_1)\phi_j(r_2) - \phi_i(r_2)\phi_j(r_1) \right\} \left[ \begin{array}{c} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \\ \beta(1)\beta(2) \end{array} \right]
\]

Effective spin Hamiltonian ($H_{\text{eff}}$) which gives the same eigenvalues as original Hamiltonian:

\[
H_{\text{eff}} = \frac{1}{4} (E_s + 3E_t) - (E_s - E_t) S_1 \cdot S_2
\]

Heisenberg Model:

\[
H_{\text{Heisenberg}} = -2J_{ij} \sum_{i<j} S_i \cdot S_j
\]

2\(J \equiv E_s - E_a\)

- direct exchange energy

\(J_{ij} > 0\): FM (Coulomb interaction)

\(J_{ij} < 0\): AFM (solid $^3$He)
Early studies of exchange interactions in solid $^3$He (1960s)

Volume dependence of $J$

$|J| \propto V^{18}$

$J \approx -1$ mK at melting pressure

$T_2$ in NMR

Magnetic susceptibility


antiferromagnetic

$\theta_W (= -4J) < 0$

R.A. Guyer, R.C. Richardson and L.I. Zane,
Rev. Mod. Phys. 43, 532 (1971)

strong volume dependence

$|J| \propto V^{18}$

exchange narrowing

$T_2 \propto |J|$
Early studies of exchange interactions in solid $^3$He (II)

Specific heat

- exchange term: $C_V \propto J^2/T^2$
- phonon term: $C_V \propto T^3$

Isochoric pressure

- exchange term: $P_V \propto (\partial |J|/\partial V)/T$
- phonon term: $P_V \propto T^4$

Large energy separation $\hbar \omega_D/J \approx 10^4$

D.S. Greywall, PRB 15, 2604 (1977)

Nuclear Spin Ordering in solid $^3$He at $T \approx 1$ mK

- Strong first-order AFM transition at $T_N = 1$ mK
  $\Delta S = 0.43 \ln 2$ (not spin-Peierls transition)

- AFM spin-waves in ordered phase
  meting pressure $\propto T^4$ ($C \propto T^3$)

- Anomalous behaviour in paramagnetic phase


Magnetization

\[ V = 24.2 \text{ cm}^3/\text{mol} \]
\[ B = 50 \text{ mT} \]

T.C. Prewitt and J.M. Goodkind, PRL 39, 1283 (1977)

Specific heat

D.S. Greywall and P.A. Busch, PRB 36, 6853 (1987)
Nuclear Spin Ordering in solid $^3$He at $T \approx 1 \text{ mK}$

**Isochoric pressure**

$24.19 \text{ cm}^3/\text{mole}$

$B = 28 \text{ mT}$

T. Mamiya et al., PRL 47, 1304 (1981)

**Melting pressure**

**U2D2 Phase**


AFM resonance in spin ordered phase for single crystal

- Large zero-field resonance frequency
  \( \Rightarrow \) non-cubic spin structure (1 kHz for cubic)

- Only one resonance at \( B = 0 \)

- Three pairs of mode at \( B \neq 0 \)
  \( \Rightarrow \) easy-plane (uniaxial symmetry)
  \( \Rightarrow \) three magnetic domains

- **U2D2 phase** (four sublattices)

**OCF eqs. to describe spin dynamics in U2D2 phase**

\[
\begin{align*}
\dot{S} &= \gamma S \times H - l(d \cdot l)(d \times l) \\
\dot{d} &= d \times \left( \gamma H - \frac{\lambda^2}{\chi_\perp} S \right)
\end{align*}
\]

\( S \): total spin \( // H \)
\( d \): unit vector \( // \) sublattice magnetization \( <S_i> \)
\( l \): anisotropy axis \( // (1, 0, 0), (0, 1, 0), (0, 0, 1) \)
\( E_D = \frac{1}{2} \lambda (l \cdot d)^2 \): dipolar energy
\( \chi_\perp \): perpendicular magnetic susceptibility

\( d \perp l, d \perp H \) in equilibrium, \( d \perp l, d \perp H \)
Magnetic phase diagram

Two AFM ordered phases:

**HFP** ($B \geq 0.45$ T) CNAF phase
- large magnetization ($M \geq 0.6$ $M_{\text{sat}}$)
- positive ($dT_c/dB$)

**LFP** ($B \leq 0.45$ T) U2D2 phase

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D.D. Osheroff et al., PRL 58, 2458 (1987)

A. Sawada et al., PRL 56, 1587 (1986)
1. Large **four-spin exchange** interaction can explain strong 1st-order transition

\[
F = E - TS = F_0 + \left( 2k_B T - a \right) M^2 + \left( \frac{4}{3} k_B T - b \right) M^4 + \cdots \\

b \approx J_4 (\sigma_i \cdot \sigma_j) (\sigma_k \cdot \sigma_1)
\]

2. Competing **FM three-spin** and **AFM four-spin exchanges** can explain magnetic phase diagram

**Two parameter model:**
- three-spin exchange \((T_1) \approx -0.13\) mK
- planar four-spin exchange \((K_P) \approx -0.39\) mK

Ring exchanges are dominant!
Two-, Three-, and Four-Atom Exchange Effects in bcc $^3$He

J. H. Hetherington and F. D. C. Willard

Physics Department, Michigan State University, East Lansing, Michigan 48824

(Received 22 September 1975)

We have made mean-field calculations with a Hamiltonian obtained from two-, three-, and four-atom exchange in bcc solid $^3$He. We are able to fit the high-temperature experiments as well as the phase diagram of Kummer et al. at low temperatures. We find two kinds of antiferromagnetic phases as suggested by Kummer's experiments.

J.H. Hetherington and F.D.C. Willard,
Ring spin exchange (RE) Hamiltonian


\[ H_{\text{eff}} = \sum_{P} (-1)^{P} P J_{P} P \]

*P*: permutation operator

*J*<sub>P</sub>: exchange energy

**Two-spin exchange** (AFM)

\[ P_{1} = P_{ij} = \frac{1}{2} (1 + \sigma_{i} \cdot \sigma_{j}) \quad \rightarrow \text{Heisenberg type} \]

**Three-spin exchange** (FM)

\[ P_{ijk} = P_{ij} P_{ij} = \frac{1}{4} (1 + \sigma_{i} \cdot \sigma_{j}) (1 + \sigma_{i} \cdot \sigma_{k}) \]

\[ P_{2} = P_{ijk} + P_{ijk}^{-1} = \frac{1}{2} (1 + \sigma_{i} \cdot \sigma_{j} + \sigma_{j} \cdot \sigma_{k} + \sigma_{k} \cdot \sigma_{i}) \quad \uparrow \text{Heisenberg type} \]

**Four-spin exchange** (AFM)

\[ P_{ijkl} = P_{ijk} P_{il} \]

\[ P_{3} = P_{ijkl} + P_{ijkl}^{-1} = \frac{1}{4} \left( 1 + \sum_{\mu<\nu} \sigma_{\mu} \cdot \sigma_{\nu} + G_{ijkl} \right) \]

\[ G_{ijkl} = (\sigma_{i} \cdot \sigma_{j})(\sigma_{k} \cdot \sigma_{l}) + (\sigma_{i} \cdot \sigma_{l})(\sigma_{j} \cdot \sigma_{k}) - (\sigma_{i} \cdot \sigma_{k})(\sigma_{j} \cdot \sigma_{l}) \quad \leftrightarrow \text{new terms} \]
Ring spin exchange (RE) Hamiltonian

**Five-spin exchange (FM)**

\[ P_{ijklm} = P_{ijkl} P_{im} \]

\[ P_5 = P_{ijklm} + P_{ijklm}^{-1} = \frac{1}{8} \left( 1 + \sum_{\mu < \nu} \sigma_\mu \cdot \sigma_\nu + \sum_{\mu < \nu < \eta < \epsilon} G_{\mu \nu \eta \epsilon} \right) \]

\[ \uparrow \text{4-spin terms} \]

**Six-spin exchange (AFM)**

\[ P_{ijklmn} = P_{ijklm} P_{in} \]

\[ P_6 = P_{ijklmn} + P_{ijklmn}^{-1} = \frac{1}{16} \left( 1 + \sum_{\mu < \nu} \sigma_\mu \cdot \sigma_\nu + \sum_{\mu < \nu < \eta < \epsilon} G_{\mu \nu \eta \epsilon} + S_{ijklmn} \right) \]

\[ S_{ijklmn} = \left\{ (\sigma_i \cdot \sigma_j)(\sigma_k \cdot \sigma_l)(\sigma_m \cdot \sigma_n) + (\sigma_j \cdot \sigma_k)(\sigma_l \cdot \sigma_m)(\sigma_n \cdot \sigma_i) + \cdots \right\} \]

\[ \uparrow \text{new terms} \]
Ring exchange processes

H. Godfrin and D.D. Osheroff, PRB 38, 4492 (1988)
WKB calculations of RE frequencies

- Path-integral Monte Carlo (PIMC) calculations
  D.M. Ceperley and G. Jacucci, PRL 58, 1648 (1987)

\[ J_P = C_P s_P \exp\left(-\frac{A_P}{g}\right) \]

- \( A_P \approx L \sqrt{V_{\text{max}}} \) : action
- \( g = \hbar \left(8m\sigma^2\varepsilon\right)^{-1/2} \left(a/\sigma\right)^5 \)
- \( C_P \): prefactor
- \( s_P \): symmetry factor
- \( \varepsilon, \sigma \): parameters in L-J potential
- \( a \): lattice constant

Different MSEs should have different Grüneisen constants.
WKB calculations of RE frequencies

2D systems with $r^{-12}$ potential

M. Roger, PRB 30, 6432 (1984)

$J_P = C_P s_P \exp\left(-A_P/g\right)$,

$A_P \approx L \sqrt{V_{\text{max}}}$

$\Gamma(J_P) = \frac{\partial \ln J_P}{\partial \ln V} \approx \frac{5A_P}{3g}$

**Two-spin**

$V_{\text{max}} = 52.5$

$L^2 = 1.30$

$A_P = 8.25$

$N = 16$

**Three-spin**

$V_{\text{max}} = 41.4$

$L^2 = 1.10$

$A_P = 6.73$

$N = 18$

**Four-spin**

$V_{\text{max}} = 44.9$

$L^2 = 1.28$

$A_P = 7.60$

$N = 16$

**Six-spin**

$V_{\text{max}} = 35.9$

$L^2 = 1.63$

$A_P = 7.64$

$N = 24$

**Twelve-spin**

$V_{\text{max}} = 65.7$

$L^2 = 3.08$

$A_P = 14.21$

$N = 30$
Path-integral Monte Carlo calculations of RE frequencies

D.M. Ceperley and G. Jacucci, PRL 58, 1648 (1987)

Density matrix $ρ$ of $N (= 128)$ distinguishable particles:

$$ρ(R,R';β) = \sum_n e^{-βE_n}\phi_n(R)\phi_n(R'), \quad β = 1/k_B T$$

$J_P$ are calculated from

$$F_P(β) \equiv -\frac{ρ(Z,PZ;β)}{ρ(Z,Z;β)} = \tanh\{J_P(β - β_P)\}$$

$$= \frac{\int dR_1\cdots dR_{M-1} ρ(Z,R_1;τ) ρ(R_1,R_2;τ) \cdots ρ(R_{M-1},PZ;τ)}{\int dR_1\cdots dR_{M-1} ρ(Z,R_1;τ) ρ(R_1,R_2;τ) \cdots ρ(R_{M-1},Z;τ)},$$

where $\exp(J_Pβ_P) = \phi_1(Z)/\phi_0(Z)$ and $τ = β/M$.

<table>
<thead>
<tr>
<th>Volume (cm$^3$/mole)</th>
<th>$ρ$ type</th>
<th>$J_P$ (MC) ($μK$)</th>
<th>$J_P$ (MC) (mK)</th>
<th>$J_P$ (MEM) (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(1) nn</td>
<td>15 (± 13%)</td>
<td>0.46 (± 7%)</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>2(2) nnn</td>
<td></td>
<td>0.065 (± 10%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3(112) triplet</td>
<td>4 (± 20%)</td>
<td>0.19 (± 10%)</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>4(1$^1$,23) planar</td>
<td>6 (± 30%)</td>
<td>0.27 (± 10%)</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>4(1$^1$,22) folded</td>
<td></td>
<td>0.027 (± 18%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4(1122;31)</td>
<td></td>
<td>0.006 (± 25%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4(1212;11)</td>
<td></td>
<td>0.0005 (± 45%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4(1212;14)</td>
<td></td>
<td>0.011 (± 30%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4(2$^1$,33) square</td>
<td></td>
<td>0.0019 (± 30%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6(1$^1$,3$^1$,4$^1$)</td>
<td>0.036</td>
<td>0.36 (± 30%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6(1$^1$,523,523;417)</td>
<td></td>
<td>0.022 (± 35%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Consistent with WKB results

$$J_P = C_P s_P \exp(-A_P/g)$$

M. Roger and J.H. Hetherington, PRB 41, 200 (1990)
Scaling behaviour in volume

Why do $J_\text{Ps}$ in RE model have all similar Grüneisen constant!??
Alternative models for magnetism of solid $^3$He

**Vacancy model**
A.F. Andreev et al., JETP Lett. 26, 36 (1978)

- FM polaron due to zero-point vacancy (ZPV)
  - Nagaoka theorem for bipartite lattice (bcc)
  - absence of upper critical field ($B_{c2}$) for HFP

**Spin-Peierls model**
R.A. Guyer and P. Kumar, JLTP 47, 321 (1982)

- Anisotropic lattice distortion $\approx 10^{-2}$
  - no explanation for HFP
  - $|J| (\approx 1 \text{ mK})$ is too small compared to $\theta_D (\approx 10 \text{ K}).$
Ferromagnetic spin polarons

First of all, ZPV (or hole) should exist in solid $^3$He.


⇒ S. Miyashita (O-03)

Nagaoka theorem requires FM ground state for bipartite lattices with single hole,

Y. Nagaoka, PR 147, 392 (1966)

because hopping back of a hole to original position always results in odd particle permutation.

FM plaron is created in AFM background at $T = 0$. 

Magnetic phase diagram of bcc $^3$He (recent progress)

- **Reentrant** PP-HFP phase boundary even at melting density (24.2 cm$^3$/mol)
  - $\Rightarrow$ inconsistent with ZPV model
- Too low $T_c^{\text{max}}$ compared to $\mu B_{c2}(0)/k_B$
- $T_c \rightarrow 0$ as $B \rightarrow 0$
  - $\Rightarrow$ highly frustrated

H. Fukuyama et al., cond-mat/0505177
Comparisons between experiments and theories

H. Fukuyama et al., cond-mat/0505177
H. Fukuyama et al., PRL 67, 1274 (1991)

• Different Grüneisen constants for $B_{c2}(0)$ and $B_{c1}(0)$:
  $B_{c2}(0) = 19.7 \pm 0.4$ T
  $\Gamma\{B_{c2}(0)\} = 19.9 \pm 0.2$

• PIMC calculation:
  $B_{c2}(0) = 18.9$ T (consistent with exp.)
  $\Gamma\{B_{c2}(0)\} = 18.1$ (inconsistent with exp.)

• Positive curvature of $M(T)$ near $B_{c2}(0)$
  ⇒ slow convergence of series of higher exchanges
Antiferromagnetic spin waves in U2D2 phase (LFP)

At low $T \ll T_N$,

$$C(T) = \frac{2n\pi^2 V k_B}{15} \left( \frac{k_B T}{\hbar v} \right)^3,$$  

$$\frac{1}{v^3} = \frac{1}{v/\nu_{\perp}^2}$$

$v$: mean spin-wave velocity

$n$: number of modes ($= 2$ for LFP)

$V$: molar volume

$$v = \frac{a}{\hbar} 2(2J_1 + J_2 + 4J_3 + 3K_P)^{1/2} (K_F - J_2)^{1/3} (J_2 + 4J_3 - K_F - \frac{J_1^2}{3K_P + K_F})^{1/6}$$


Spin wave spectrum

$T_1 = 0.1$ mK

$K_P = 0.355$ mK

Melting pressure

$$\frac{dP}{dT} = \frac{S_L - S_S}{V_L - V_S} \approx -\frac{S_S}{V_L - V_S}$$

$$\Delta P \propto T^4$$

$$\Rightarrow \quad v = 7.5 \text{ cm/s}$$


Roger, Hetherington and Delrieu, Rev. Mod. Phys. 55, 1 (1983)
Linear spin-wave calculation is ill defined in HFP at low fields, but is OK in LFP.

Higher frustration in non-collinear CNAF than in collinear U2D2 phase?
Ferromagnetism in hcp $^3$He

- Three spin exchanges are dominant and introduce ferromagnetism in hcp phase being consistent with WKB predictions.
- Possible ferromagnetic orderings: $T_c \leq 20 \, \mu K$.

### WKB calculations of MSE frequencies in hcp $^3$He


<table>
<thead>
<tr>
<th>$J_P$</th>
<th>$V_M$</th>
<th>$L^2$</th>
<th>$(V_M)^{1/2}L$</th>
<th>$J_P/J_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_T$ three</td>
<td>53.7</td>
<td>1.00</td>
<td>7.33</td>
<td>1</td>
</tr>
<tr>
<td>$J_T'$ three</td>
<td>60</td>
<td>1.00</td>
<td>7.75</td>
<td>0.45</td>
</tr>
<tr>
<td>$K'^2_{12}$ four</td>
<td>57</td>
<td>1.14</td>
<td>8.09</td>
<td>0.23</td>
</tr>
<tr>
<td>$J_2$ two</td>
<td>79</td>
<td>0.935</td>
<td>8.60</td>
<td>0.08</td>
</tr>
<tr>
<td>$J_T^*$ three</td>
<td>76</td>
<td>1.02</td>
<td>8.83</td>
<td>0.06</td>
</tr>
<tr>
<td>$K'$ four</td>
<td>67</td>
<td>1.20</td>
<td>9.00</td>
<td>0.04</td>
</tr>
<tr>
<td>$K'$ four</td>
<td>69</td>
<td>1.27</td>
<td>9.38</td>
<td>0.02</td>
</tr>
<tr>
<td>$J_2$ two</td>
<td>70</td>
<td>1.30</td>
<td>9.54</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Solid $^3$He: an ideal quantum spin system

**Simplicity**
- No impurities (superclean!)
- Nuclear-spin system
  - no spin-orbit coupling
- Isotropic exchange interactions ($J \approx 1$ mK)
  - atom-atom exchanges
    - large zero-point motion
  - $^1S$ closed electronic shell
- Large energy separation
  \[ \hbar \omega_d/J \approx 10^4, \ E_{d-d}/J \approx 10^{-5} \]
- Quantum spin ($S = 1/2$)

**Highly tunable**
- Dimension
  - 3D (bcc or hcp), 2D (triangular), 0D (cluster)
- Frustration
  - competing ring exchanges
    - AFM: even number
    - FM: odd number
- Geometrical
  - bipartite: bcc
  - non-bipartite: triangular, hcp
- Compressible
  \[ K \approx 5 \times 10^{-3} \ \text{bar}^{-1} \ \text{near M. C.} \]
Future prospects of ring exchange model in 3D solid $^3$He

Experimental magnetic properties of bcc $^3$He can be explained by theoretical RE frequencies based on first principles even quantitatively within 30 %.

1. Anomalous softening of spin wave velocity in HFP. ⇒ Y. Okamoto (P-14)
2. Observation of optical spin wave mode in LFP. ⇒ S. Sasaki (O-02)
3. Detailed test of the model in terms of Grüneisen tensors. ⇒ S. Sasaki (O-02)
4. Neutron diffraction of the ordered phases.
5. Impurity effects.
6. Size effects.

Other aspects as a quantum crystal

2. Nucleation ⇒ T. Tanaka (P-13)
Related systems with ring exchanges

1. 2D $^3\text{He}$ $\Rightarrow$ K. Kubo (O-04), M. Morishita (O-05), J. Saunders (O-12), S. Murakawa (O-13), T. Takagi (O-14), H. Ishimoto (O-23)

2. Spin ladders, Cuprates, Transition metal oxides near Mott transition $\Rightarrow$ T. Sakai (O-06), T. Momoi (O-25)

3. 2D electron systems (Si-MOS, …) $\Rightarrow$ K. Toyama (P-01)

Does the $(t/U)$ expansion of Hubbard model:

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i \sigma}^\dagger c_{j \sigma} + U \sum_i n_{i \uparrow} n_{i \downarrow}$$

gives

$$J_P \approx t \left( \frac{t}{U} \right)^P$$

Here, $J_P$ are ring exchanges.

A.H. MacDonald, S. M. Gurvin and D. Yoshioka, PRB 37, 9753 (1988)
Magnetism of NiS$_2$

- located near Mott transition ($U \approx t$):
  \[ H = \sum_{\sigma} \sum_{i,j} t_{ij} a_i^+ a_j + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \]
  metal $\rightarrow$ insulator transition at $P = 3.5$ GPa
- coexistence of three phases ($T_c \leq 29$ K):
  AF phase (FCC-I)
  AF phase (FCC-II)
  WF (weak ferromagnetic) phase ($0.01 \mu_B$)
- first order transition to the coexistence phase
- rapid decrease of $T_c$ by substituting S atom with Se

**Four-spin interactions ($t^d$-order perturbation)**

**Impurity effect**
T. Miyadai et al., JPSJ 52, 3308 (1983)

**Neutron diffraction**
T. Miyadai et al., JPSJ 38, 115 (1975)