Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi

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Outline

• Motivation
• Why CeNi?
• Structural behavior of CeNi under pressure
• Magnetic dynamics of CeNi before and after structural transition
• Conclusions
Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi

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Motivation

The main problem of interest:

mechanisms underlining the pressure-induced first-order structural phase transition with volume jump in f-electron systems

The problem is closely related to understanding crossover between the local moment and itinerant f electron behavior.

The most famous examples are:

• the isostructural volume-collapse $\gamma \rightarrow \alpha$ transition in Ce metal
• $\delta \rightarrow \alpha$ transformation in plutonium metal ($\delta \rightarrow \alpha'$ in fcc Pu-Ga alloy)
**Isosctructural volume-collapse $\gamma \rightarrow \alpha$ transition in Ce metal**

$\Delta V/V \sim 15-17\%$

Atomic volume $V = a^3/4$ of Ce vs. pressure at room temperature. $a$ is the crystal lattice parameters.


Red signs – VNIITF data.

(a) dc bulk magnetic susceptibility $\chi(T)$ for Ce$_{0.721}$Th$_{0.269}$.

(b) The effective moment $\mu_{\text{eff}} = T\chi/C$ should saturate to unity at high $T$.

S.M. Shapiro et al., PRB 16 (1977) 2225.

Replacement of the normal Curie-Weiss $T$-dependence in $\chi(T)$ of $\gamma$ phase (indicative of a local moment behavior) by a practically $T$-independent susceptibility in $\alpha$-Ce (suggesting a quenched moment state).
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$\delta \rightarrow \alpha'$ transformation in fcc Pu-Ga alloy


Volume difference between $\alpha$- and $\delta$- phases is $\sim 25\%$
**Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi**

\[ \delta \rightarrow \alpha' \] transformation in fcc Pu-Ga alloy

- Pressure-induced \( \delta \rightarrow \alpha' \) transformation in fcc Pu-Ga alloys [S. Hecker, 2011].

- \( \delta \) phase directly transforms to \( \alpha' \)

- X-ray diffraction pattern of pressure-induced \( \delta \rightarrow \alpha' \) transition in Pu-3.3%at.Ga [A. Schwartz et al., Progress in Materials Science, 2009]

- Both \( \alpha' \)- and \( \gamma' \)- phases arise simultaneously under pressure

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Many features of this transition still have no explanation, including stabilization of the fcc phase by alloying different elements, influence of defects and strains on the transformation etc.
Why CeNi?

• CeNi is an intermediate-valence system experiencing pressure-induced structural instability [D. Gignoux, F. Givord, and R. Lemaire, J. Less-Common Metals 94 (1983) 165].

Magnetic susceptibility vs. temperature for CeNi (●) in a field of 50 kOe applied along the a, b, and c axes of the orthorhombic structure and the susceptibility of polycrystalline LaNi (○).

Specific heat vs. T for CeNi and LaNi. Inset: ΔC= C_{CeNi} - C_{LaNi}.

Thermal variation of resistivity $\rho_{Ce} = \rho_{CeNi} - \rho_{LaNi}$ along the a and c axes.
**Why CeNi?**

CeNi has the CrB-type orthorhombic crystal structure (space group Cmcm) repeatedly appearing in rare-earth and actinide metals under pressure, e.g., \(\alpha'^{-}\text{Ce}, \text{Pa}, \text{Nd}, \text{Pr}, \text{Am IV}, \text{and } \alpha^{-}\text{U} \).

\[a = 3.77 \text{ Å}, \quad b = 10.46 \text{ Å}, \quad c = 4.37 \text{ Å}\]

Ce: 4c (0, 0.139, 1/4)

Ni: 4c (0, 0.428, 1/4)

Why CeNi?

• CeNi experiences pressure-induced first-order structural phase transition.

The structure of CeNi high pressure phase remained unknown for a long time (since 1985). Study of the structural transition in this compound can be useful to better understand the behavior of similar structures under pressure.
Why CeNi?

• As soon as the Ce valence in intermediate-valence CeNi differs significantly from integer value, one can expect the volume-collapse structural phase transition to shift the system towards the itinerant (bonding) f electron behavior (in this sense structural transition in CeNi can be considered as an analog of $\delta \rightarrow \alpha'$ transformation in plutonium).

The aim of this work is to determine the crystal structure of the CeNi high pressure phase using x-ray and neutron powder diffraction and to study the variation of magnetic excitation spectrum in CeNi due to structural transition by means of INS technique.
**Experimental**

**Structural investigations:**

powdered CeNi sample (natural mixture of Ni isotopes)

high-pressure synchrotron x-ray measurements, beamline 17-BM-B, APS (ANL)

T = 298 K, pressure up to 7.8 GPa

neutron powder diffraction, SNS (ORNL) SNAP diffractometer

T = 100 K, pressure up to 5.05 GPa

details: A. Mirmelstein et al., PRB 92, 054102 (2015)

**Inelastic neutron scattering SNS, ORNL:**

polycrystalline CeNi sample of ~3 g in mass, $^{60}$Ni isotope (enrichment ~99%)

$^{60}$Ni nuclear cross section $\sigma_S = 1.0$ b

natural isotope mixture compared to $\sigma_S = 18.5$ b

magnetic cross section of Ce$^{3+}$ ions $\sigma_M \approx 3.7$ b

INS spectra of CeNi were measured using fine-resolution Fermi chopper spectrometer SEQUOIA, T = 20 K, ambient pressure, P = 0.4 GPa

Magnetic formfactor was measured with ARCS (wide angular-range chopper spectrometer) instrument

T = 20 K, ambient pressure, P = 0.45 GPa

Pressure was generated using the Al pressure cell with He gas as a pressure transmitting medium
**Structure of CeNi high pressure-phase**

![Diagram](image)

**P-T phase diagram of CeNi as follows from the present diffraction (green and brown squares), magnetic (yellow triangles and red circles), and specific heat measurements. Blue solid line – empirical transition line suggested by Gignoux and Voiron (1985).**

At room temperature:

First structural transformation occurs around $P \sim 1$ GPa.

CrB ($Cmcm$ space group) structure transforms to the FeB-type of structure ($Pnma$ space group). $\Delta V/V=1.3\%$ at $P = 1.17$ GPa

Second transformation occurs around 5 GPa

FeB $\rightarrow Pnma$-based mixed phase state FeB+$3a_{FeB}$

( explanation below)
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CeNi Low Pressure (LP) phase

- **CrB-type Cmcm**
- $P=0.7$ GPa (below transition)
- $a = 3.771(2)$ Å, $b = 10.529(8)$ Å, $c = 4.366(2)$ Å
- Ce: 4c 0, 0.14(1), 1/4
- Ni: 4c 0, 0.42(1), 1/4

CeNi High Pressure (HP) phase

- **FeB-type Pnma**
- $P=4.2$ GPa
- $a = 7.161(5)$ Å, $b = 4.390(4)$ Å, $c = 5.086(4)$ Å
- Ce: 4c 0.13(1), 1/4, 0.20(1)
- Ni: 4c 0.09(1), 1/4, 0.66(1)

The FeB structure is typical for the RNi compounds where R is the rare-earth metal from the second half of the lanthanide series, while light lanthanides, including cerium, form the crystal lattice of the CrB type [A.E. Dwight, R.A. Conner, Jr., J.W. Downey, Acta Cryst. 18, 837 (1965)]

Both the FeB and CrB structural types contain a common structural unit, the trigonal prism, which is stacked differently to form either structure [R. Lemaire and D. Paccard, Journal of the Less-Common Metals 21, 403(1970)].
If the z value of the 4c sites in the Pnma structure goes to zero, one obtains the higher-symmetry Cmcm structure.
**Structure of CeNi high pressure-phase**

At $T = 100$ K:

Pure FeB Pnma structure was not found. At $P$ above 1 GPa the neutron powder diffraction patterns are described by a new orthorhombic cell with crystal lattice parameters $a = 3 \times a_{FeB}$; $b = b_{FeB}$; $c = c_{FeB}$

$$3 \times a_{FeB}^{Pnma}$$

This structure is similar to the structure of quenched modification of the TbNi compound [R. Lemaire and D. Paccard, Journal of the Less-Common Metals 21, 403(1970)]

$\Delta V/V = 7.9\%$ at $P = 0.96$ GPa

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$P$-$T$ phase diagram of CeNi as follows from the present diffraction (green and brown squares), magnetic (yellow triangles and red circles), and specific heat measurements. Blue solid line – empirical transition line suggested by Gignoux and Voiron (1985).
**Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi**

**Structure of CeNi high pressure-phase**


\[
\begin{align*}
    a_{TbNi} &= 3a_{FeB} \\
    b_{TbNi} &= c_{FeB} \\
    c_{TbNi} &= c_{FeB}
\end{align*}
\]

**P-T phase diagram of CeNi**

These previous experiments seem to confirm two transitions for both low and room temperature

**Thermopower vs. pressure for CeNi at T=300 K**

A. Mirmelstein et al. (2007)

**Specific heat coefficient \( \gamma \) vs. pressure for CeNi**

Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi

Equation of State for CeNi at $T = 300\, \text{K}$ and $T = 100\, \text{K}$.

Solid lines are the results of fitting the measured unit cell volume to a third-order Birch-Murnaghan EOS [F. Murnaghan, PNAS 30, 244 (1944), F. Birch, Phys. Rev. 71, 809 (1947)].
Фазовые переходы с коллапсом объема в f-электронных системах: CeNi

Парциальные плотности состояний для (а) CeNi Cmcm фазы при нормальном давлении, (b) Cmcm фазы при $P = 1$ ГПа и (c) Pnma фазы при $P = 1$ ГПа.

На вставках – те же DOS вблизи $E_F$ в увеличенном масштабе.

Signature of increased f-d hybridization can be seen in panel (c).
**Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi**

**Structure of CeNi high pressure-phase: Pnma symmetry**

**DFT calculations (VASP)**

The relative energies as function of pressure for LP *Cmcm* (circles) and HP *Pnma* (diamonds) structure as obtained from DFT calculations. Arrow indicates the structural transition at pressure $P = 0.94$ GPa.

DFT (LDA) calculations confirm the stability of the *Cmcm* CeNi crystal structure at ambient pressure down to the lowest temperature.

At the pressure value above 1 GPa the *Pnma* structure becomes preferable.

Interatomic distances (with respect to a central Ce ion):

- **Cmcm**:  
  1st coordination sphere – 7 Ni neighbors  
  $2 \times R_1 = 2.938 \, \text{Å}$, $4 \times R_2 = 2.948 \, \text{Å}$, $1 \times R_3 = 3.011 \, \text{Å}$.  
  2nd coordination sphere – 8 Ce neighbors  
  $2 \times R_4 = 3.601 \, \text{Å}$, $4 \times R_5 = 3.752 \, \text{Å}$, $2 \times R_6 (LP) = 3.771 \, \text{Å}$

- **Pnma**:  
  1st coordination sphere – 6 Ni neighbors  
  $1 \times R_1 = 2.357 \, \text{Å}$, $1 \times R_2 = 2.761 \, \text{Å}$, $2 \times R_3 = 2.794 \, \text{Å}$, $2 \times R_4 = 2.980$.  
  2nd coordination sphere – 8 Ce neighbors  
  $2 \times R_5 = 3.525 \, \text{Å}$, $2 \times R_6 = 3.611 \, \text{Å}$, $4 \times R_7 = 3.773 \, \text{Å}$.

- **R-Ni distances ↓ ⇒ 4f-Ni3d hybridization is expected to increase**
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Magnetic excitation spectrum of CeNi

The magnetic susceptibility vs. temperature (left) and inverse magnetic susceptibility vs. temperature (right) for two powder samples of CeNi.

Red curves correspond to the Curie-Weiss law with the effective magnetic moment of free Ce$^{3+}$ ion $p = g[(J(J+1))]^{1/2} = 2.53$ (J=5/2). ORNL sample was prepared for the INS experiments using $^{60}$Ni isotope. VNIITF sample was prepared for previously published magnetic measurements.

A. Mirmelstein et al., JNM 385, 57 (2009)

Anomalous upturn of $\chi(T)$ below 20 K has, most probably, an intrinsic origin connected presumably with coherent f-d hybridization [V.R. Fanelli et al., J. Phys.: Condens. Matter 26, 225602 (2014); J. Aarts et al., Solid State Commun. 56, 523 (1985)]
Magnetic excitation spectrum of CeNi

\[ S_{\text{mag}}(Q, E, T) \sim |F(Q)|^2 \frac{E}{1 - \exp(-E/k_B T)} \frac{\Gamma/2}{(\Gamma/2)^2 + (E - E_0)^2} \]

\( \Gamma \) is the full width at half maximum (FWHM) of Lorentzian spectral component. \( E_0 \) determines the characteristic energy scale of the IV system (Kondo temperature \( T_K = E_0/k_B \))

\( E_1 = 15 \pm 0.2 \) meV, \( \Gamma/2 = 3.3 \pm 0.2 \) meV
\( E_2 = 30 \pm 0.3 \) meV, \( \Gamma/2 = 3.3 \pm 0.2 \) meV
\( E_3 = 40 \pm 2 \) meV, \( \Gamma/2 = 42 \pm 3 \) meV

Magnetic scattering function \( S_{\text{mag}}(E) \) for the polycrystalline CeNi\textsuperscript{60} sample at \( T = 20 \) K and ambient pressure (no pressure cell).
**Magnetic excitation spectrum of CeNi**

CeNi\textsuperscript{60} single crystal
E. Clementyev et al. PRB 61, 6189 (2000)

Magnetic scattering function $S_{\text{mag}}(E)$ for the polycrystalline CeNi\textsuperscript{60} sample at $T = 20$ K and ambient pressure (no pressure cell).

$E_1 = 15 \pm 0.2$ meV, $\Gamma/2 = 3.3 \pm 0.2$ meV
$E_2 = 30 \pm 0.3$ meV, $\Gamma/2 = 3.3 \pm 0.2$ meV
$E_3 = 40 \pm 2$ meV, $\Gamma/2 = 42 \pm 3$ meV

E\textsubscript{1} and E\textsubscript{2} coincide with the Al PDOS maxima

The origin of two narrow spectral lines remains unknown

$E_1 \sim 18$ meV, $\Gamma/2 = 4.5 \pm 0.5$ meV
$E_2 \sim 34$ meV, $\Gamma/2 = 4.5 \pm 0.5$ meV
$E_3 \sim 46$ meV, $\Gamma/2 \sim 24$ meV

Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi
**Magnetic excitation spectrum of CeNi**

![Graph showing magnetic excitation spectrum](image)

Magnetic scattering function $S_{mag}(E)$ for the polycrystalline CeNi sample at $T = 20 \text{ K}$ and ambient pressure (no pressure cell).

- "smooth" (brown) line:
  - $E_0 = 33 \pm 3 \text{ meV}$, $\Gamma/2 = 44 \pm 5 \text{ meV}$

Polycrystalline CeNi$_{60}$, $T=12 \text{ K}$, HET (ISIS, RAL)

$E_i=150 \text{ meV}$

**Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi**

**Magnetic excitation spectrum of CeNi**

![Graph showing magnetic excitation spectrum of CeNi](image)

- **$T = 20\ \text{K},$ ambient pressure**
  - $E_0 = 33\pm2\ \text{meV}, \Gamma/2 = 44\pm3\ \text{meV}$ (smooth line)

- **$T = 20\ \text{K}, P = 0.4\ \text{GPa}$**
  - $E_0 = 50\pm2\ \text{meV}, \Gamma/2 = 55\pm3\ \text{meV}$

**Compression of CeNi leads to the increase of $T_K$ due to enhanced Ce4f-Ni3d hybridization**

Magnetic scattering function of CeNi$^{60}$ at $T = 20\ \text{K}$ and ambient pressure (blue circles) and pressure of 0.4 GPa (red triangles), i.e. before and after the structural $Cmcm\rightarrow Pnma$ phase transition.

$\text{Спектр 2016 "ПЯФ" НИЦ "КИ" 23-24 июня 2016, Гатчина}$
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Comparison with bulk measurements \([\gamma, \text{Pauli-like low-temperature } \chi_0 \sim \langle n_f \rangle / E_0]\)

CeNi magnetic measurements
A. Mirmelstein et al., JNM 385, 57 (2009)
\(\chi_0(T=30 \text{ K}, P=0) / \chi_0(T=30 \text{ K}, P=0.47 \text{ GPa}) \approx 1.33\)

CeNi specific heat
\(\gamma(P=0) / \gamma(P=0.45 \text{ GPa}) \approx 1.36, \gamma(P=0) / \gamma(P=0.6 \text{ GPa}) \approx 1.63\)

INS experiments

\(E_0(P=0.4 \text{ GPa}) / E_0(P=0) = 50/33 = 1.52\)

\(\langle n_f \rangle \approx 1 - 0.05(\text{meV}^{-1}) \times E_0\)
E.S. Clementyev and A.Mirmelstein
JETP 109, 128 (2009)

\(\langle n_f \rangle \approx 0.84 \ (P = 0), \langle n_f \rangle \approx 0.75 \ (P = 0.4 \text{ GPa})\)

\([\langle n_f \rangle / E_0(P=0)] / [\langle n_f \rangle / E_0(P=0.4 \text{ GPa})] = 1.69\)

If \(E_0(P=0) = 40 \text{ meV (broad } E_3 \text{ line)}\)

\(\langle n_f \rangle \approx 0.8(P = 0), \langle n_f \rangle \approx 0.75 (P = 0.4 \text{ GPa})\)

\([\langle n_f \rangle / E_0(P=0)] / [\langle n_f \rangle / E_0(P=0.4 \text{ GPa})] = 1.33\)

Consistent results of bulk and INS measurements
Inelastic magnetic form factor of CeNi

Dynamic magnetic response of CeNi follows the free ion Ce\(^{3+}\) magnetic form factor before and after the structural transition in spite of essential variation of Kondo temperature and spectral response broadening.

Within the energy transfer range 55 < E < 85 meV nuclear contributions becomes negligible.

Measured signal = magnetic contribution + almost Q-independent weak background.

60 < E < 80 integration window to obtain F\(^2\)(Q)

Magnetic form factor F\(^2\)(Q) of CeNi before (blue triangles) and after (black circles) pressure-induced volume-collapse structural phase transition. The calculated form factor for the free Ce\(^{3+}\) and form factor measured experimentally for \(\alpha\)-phase of metallic cerium [A.P. Murani, S.J. Levett, and J.W. Taylor, Phys. Rev. Lett. 95, 256403 (2005)] are shown for comparison.
Dynamic Magnetic Response Across the Pressure-Induced Structural Phase Transition in CeNi

Conclusions

• The pressure-induced crystal structure is shown to belong to the Pnma space group. An approximate phase diagram is suggested.

• The experimental results clearly demonstrate the increase of the characteristic energy scale of magnetic fluctuations (Kondo temperature) and the decrease of effective occupation of the 4f\(^{1}\) (J=5/2) ground state of the collapsed phase due to the enhanced Ce4f-Ni3d hybridization.

• The space distribution of magnetic density does not change under transition and remains the same as in the free Ce\(^{3+}\) ion.

4f electrons remains localized, while strongly hybridized with conducting bands, in the CeNi Pnma structure as well as in the case of \(\gamma\rightarrow\alpha\) transition in cerium.


Is \(E_{0}(T_{K})\) the only direct measure of localization/delocalization degree which can be determined experimentally?
DFT+DMFT calculations of $F(Q)$ and $\text{Im}\chi(Q,E)$ ⇒ KVC mechanism of $\gamma\rightarrow\alpha$ transition in Ce metal:
B. Chakrabarti, M.E. Pezzoli, G. Sordi, K. Haule, G. Kotliar, PRB 89 (2014) 125113
a charge self-consistent implementation, GGA functional in WIEN2K package, continuous-time quantum Monte Carlo impurity solver. $T = 116$ K, Hubbard potential $U=6$ eV, intra-atomic exchange (Hund’s coupling) $J=0.7$ eV.

![Graph 1](image1)

**Imaginary part of the local dynamic susceptibility $\text{Im}\chi(\omega)$ for $\gamma$- and $\alpha$-Ce (left). Inset: q-dependence of local static susceptibility $\chi(q, \omega = 0)$ of $\alpha$-Ce.**

Dispersionless character of $\chi(q, \omega = 0)$ proves the use of single-ion approach to calculate $F(Q)$ and is consistent with the fact that magnetic form factor does not change due to transition and keeps the form of a free Ce$^{3+}$ ion (right).

$\gamma$-phase: $T_K \sim 10$ meV, $\alpha$-phase: $T_K \sim 180$ мэВ

**Volume changes occurs due to increase in $T_K$ and enhanced f-spd hybridization**
Theory of $\gamma \rightarrow \alpha$ transition in Ce

Hybridization, $T_K$, and spin-orbit coupling in Ce

N. Lanata, Yong-Xin Yao, Cai-Zhuang Wang, Kai-Ming Ho, Jörg Schmalian, Kristjan Haule, and Gabriel Kotliar, PRL 111, 196801 (2013). LDA+GA, analog of LDA+DMFT (slave bosons to solve an impurity problem)

Total energy vs. volume (top) and P-V curves (bottom) for $U=5$ eV and $J=0.7$ eV at $T=0$. и эксперимент при $T=300$ К (внизу). Inset: the same curves for $4.5 \leq U \leq 6.5$ eV (step 0.5 eV) from the bottom to the top. Color signs – experimental data at 300 K. Horizontal lines (left bottom panel) and black signs in the inset indicate pressure corresponding to the minimum of bulk modulus $K=-VdP/dV$.

Pressure is calculated as $P = -dE/dV$. Structural transition corresponds to the minimum of $K$. At $U \leq 5.5$ eV $K$ changes sign, indicating the first order transition. At $U = 5.5$ эВ $K=0$, i.e. the second order transition.

Such a behavior is observed only in the case if spin-orbit coupling is taken into account.
Local entanglement entropy $S_f$ of the $f$ electrons serves as a measure of coupling between $f$ electrons and the rest of the environment:

$$S_f = -\text{Tr}[\rho_f \ln \rho_f]$$

$\rho_f$ – reduced density matrix of the system in the $f$ local subspace.

Crossover occurs only if SO coupling is taken into account.

In the $\alpha$-phase $S_f$ is not sensitive to the spin-orbit splitting. The local fluctuations induced in the $f$ local space by the coupling with its environment are very large.

By increasing the volume, the fluctuations between $J=5/2$ $f^1$ subspace and the other local configurations are increasingly suppressed.

The crossover points identifies the situation in which the fluctuations are sufficiently small to be hampered by the spin-orbit.

The fluctuations are generated only by the entanglement, the main source of which is the $f$-spd hybridization.
1. Different behavior of Z with and without spin-orbit coupling.
2. Different behavior of Z for 5/2 and 7/2 states at the crossover point.
5/2 electrons undergo a clear crossover towards a localized phase "disentangled" by the conduction electrons. 7/2 electrons remain screened, but rapidly disappear and are absent in the γ phase.
3. Spin-orbit coupling speeds up the formation of the 4f1 local moment (4f1 grows faster with SOC than without).

Quasiparticle renormalization weights of the 7/2 and 5/2 f electrons, 7/2 and 5/2 orbital populations, and f configuration probabilities as a function of the system volume.
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Thank you very much for your attention!
Magnetic excitation spectrum of CeNi

Magnetic scattering function of CeNi\textsuperscript{60} at ambient pressure (no cell) measured at $T = 20$ K with spectrometer SEQUOIA (blue circles) and at $T = 12$ K with ARCS instrument.
Ожидаемые для основного состояния величины энергетических компонент эффективного Гамильтониана, основное состояние которого обеспечивает решение рассматриваемой задачи. Нелокальная часть $\hat{H}$ может быть представлена в виде

$$\hat{H} = \hat{T}_{ff} + \hat{T}_{fc} + \hat{T}_{cc}$$

где $c = spd$, а три члена суммы - нелокальные перескоки между $f-f$, $f-c$ и $c-c$ электронами.

Энергии перескоков $f-f$ и $f-c$ представляют собой масштаб энергий Хаббарда и Кондо. Масштаб Кондо почти на порядок превышает масштаб Хаббарда, который $\rightarrow 0$ вблизи перехода. Это соответствует KVK модели изоструктурного перехода. Можно заключить, что основной источник связи $f$ локального пространства и его окружения – $f$-spd гибридизация. При учете СО взаимдействия энергетический масштаб Кондо уменьшается быстрее вблизи перехода, чем без учета СОВ.
Фазовые переходы с коллапсом объема в \( f \)-электронных системах: Ce, теория

Даже в \( \gamma \)-фазе, до коллапса, в основном состоянии есть примесь \( f^2 \) конфигурации, причем, судя по рисунку, ее даже больше, чем \( f^0 \).

Перераспределение между 5/2 и 7/2 состояниями – более резкий эффект вблизи перехода, чем изменение вероятностей конфигураций

При уменьшении вероятности конфигурации \( f^1 \) растет вероятность конфигурации \( f^2 \), так что \( N_f \sim 1 \), а при малом объеме \( N_f > 1 \).

Вероятность \( f^0 \) в области перехода растет незначительно.

Все вероятности, независимо от учета COB, изменяются практически монотонно в области перехода. тронов.

При \( U = U_c \sim 5.5 \) эВ – квантовая критическая точка II рода фазовой диаграммы Следовательно, металлический церий – критический элемент (J.C. Lashley et al, PRL 97 (2006) 235701)

Влияние температуры на физику \( \alpha-\gamma \) превращения: N. Lanata, Yong-Xin Yao et al., PRB 90, 161104(R) (2014)

Факторы перенормировки \( Z \) квазичастичного спектра для 7/2 и 5/2 \( f \) электронов (верхняя панель), орбитальные заселенности (в середине) и вероятности \( f \) конфигураций как функции атомного объема церия. Приведены значения этих параметров при \( U = 5 \) эВ (слева) и \( U = 6 \) эВ (справа) с учетом и без учета СО взаимодействия.

Спектина 2016 "ПИЯФ" НИЦ "КИ" 23-24 июня 2016, Гатчина
Структура фазы высокого давления CeNi
Оставалась неизвестной с 1985 г.

Основной структурный мотив: чередующиеся треугольники (тригональные призма), построенные из Ce либо Ni
Орторомбическая структура типа CrB
Пространственная группа Cmcm
$a = 3.77 \, \text{Å}, \quad b = 10.543 \, \text{Å}, \quad c = 4.37 \, \text{Å}$
Ce: 4c (0, 0.14, 1/4)
Ni: 4c (0, 0.42, 1/4)
$T = 300 \, \text{K}$

Если в Pnma (0.403, 0.25, 0.101) $z = 0 \Rightarrow Cmcm$

СrB структура типична для RNi, где R – из первой половины РЗ серии, а FeB – для R из второй половины РЗ серии
What is intermediate valence (IV)?

Energy of 4f level of isolated impurity at $T = 0$

$E_0$ – energy of unperturbed $4f^n$ level

Coulomb repulsion $\sim 5$ eV

$s$- and $p$- conducting electrons + localized $f$ electrons

Charge and spin transfer (fluctuations) between $f$- and $(s,p)$ electrons

+ hybridization

$\Gamma = \pi^2 V^2 N(E_F)$

$\Gamma < E_0$ – heavy fermions

$\Gamma \geq E_0$ – intermediate (non-integer) valence (3.2+)

$\Gamma \ll E_0$ – stable 4f shell