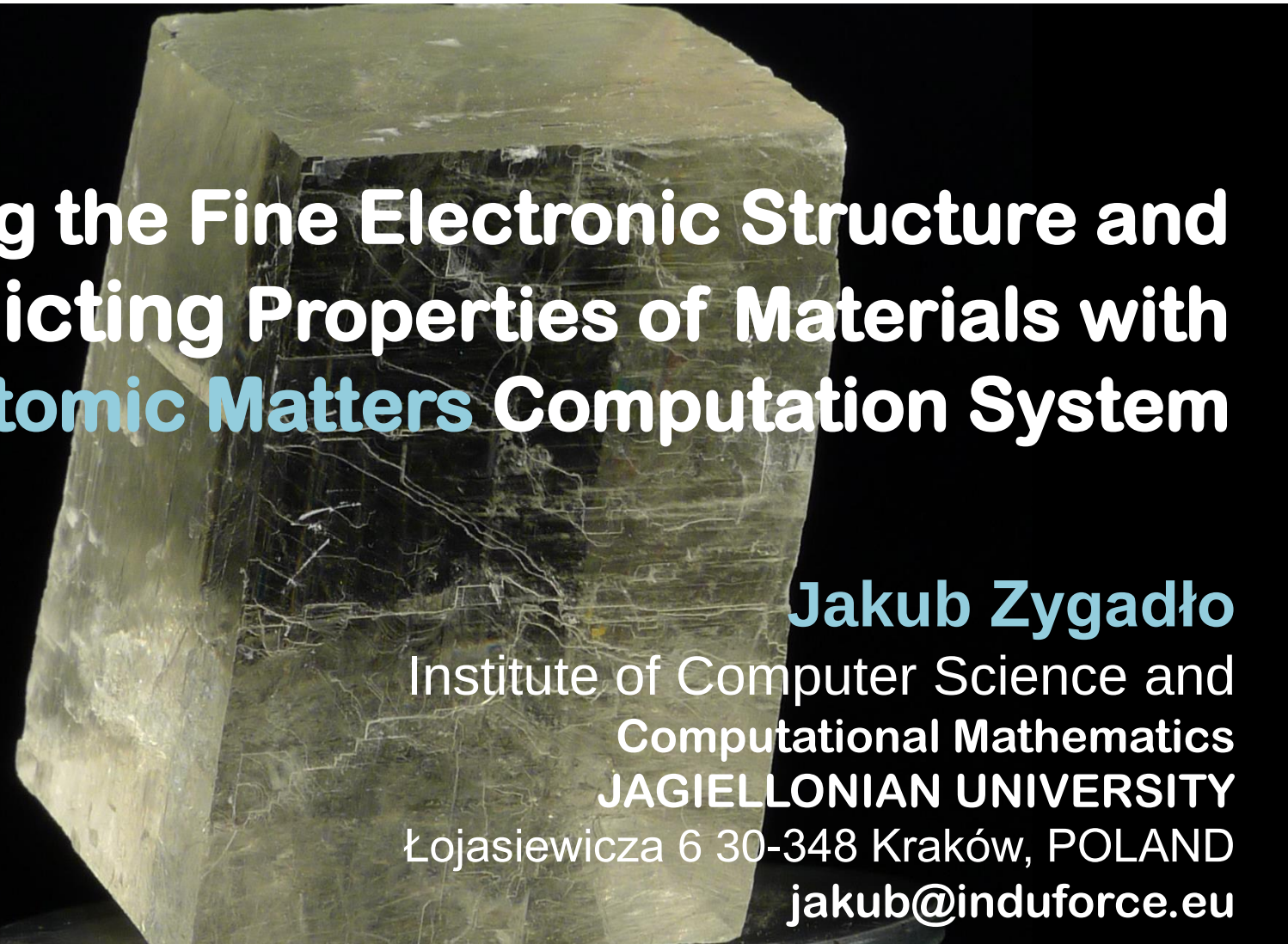
ICPMCS 2016: 18th International Conference on Physics, Mathematics and Computer Science - Dubai UAE. June 1-2, 2016

atomic matters
atomic properties and magnetism of solids



Describing the Fine Electronic Structure and Predicting Properties of Materials with Atomic Matters Computation System

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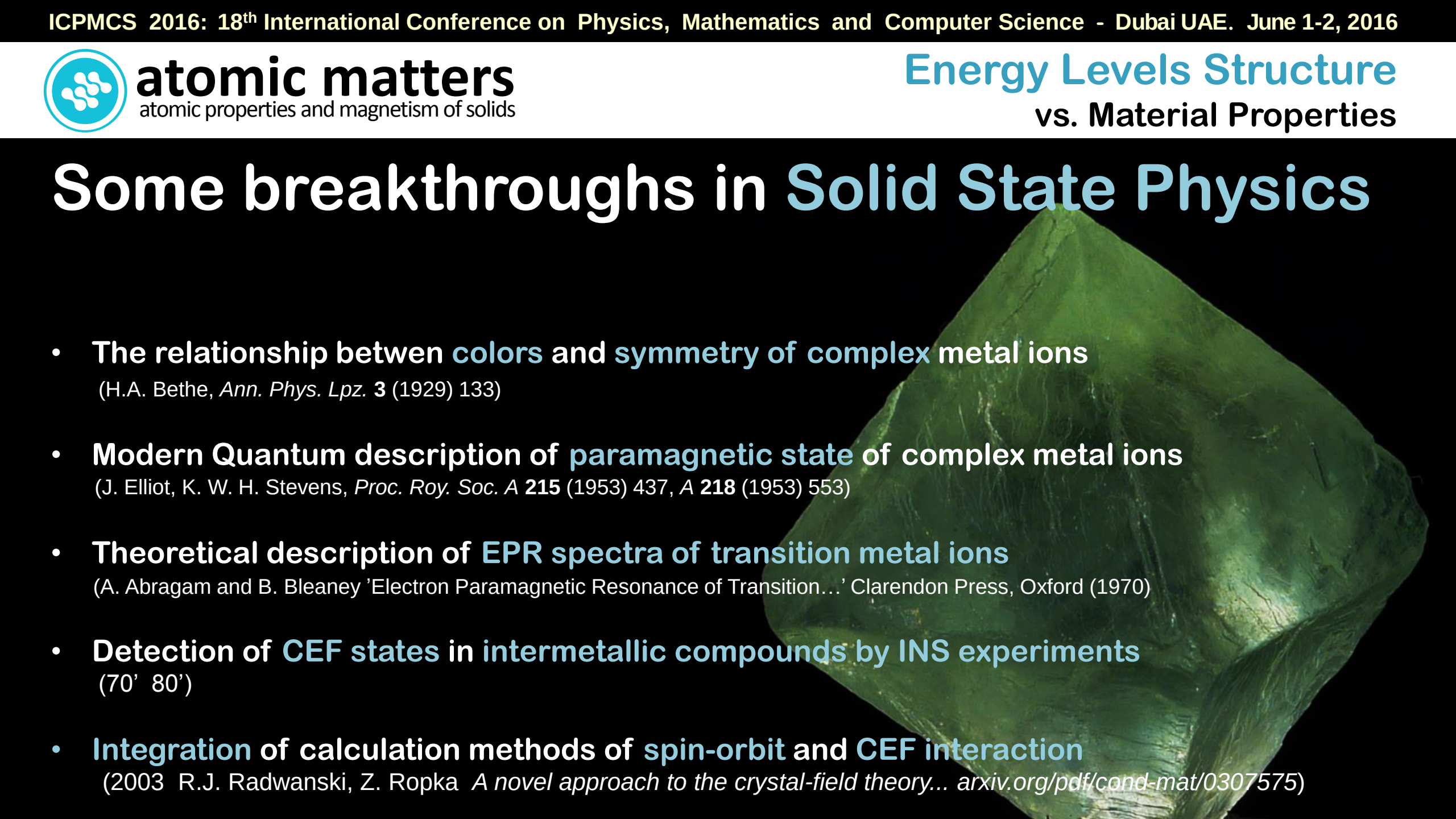
Energy Levels Structure
vs. Material Properties

Some breakthroughs in Solid State Physics



- The relationship betwen colors and symmetry of complex metal ions
  (H.A. Bethe, *Ann. Phys. Lpz.* **3** (1929) 133)
- Modern Quantum description of paramagnetic state of complex metal ions
  (J. Elliot, K. W. H. Stevens, *Proc. Roy. Soc. A* **215** (1953) 437, *A* **218** (1953) 553)
- Theoretical description of EPR spectra of transition metal ions
  (A. Abragam and B. Bleaney 'Electron Paramagnetic Resonance of Transition…' Clarendon Press, Oxford (1970)
- Detection of CEF states in intermetallic compounds by INS experiments
  (70' 80')
- Integration of calculation methods of spin-orbit and CEF interaction
  (2003 R.J. Radwanski, Z. Ropka *A novel approach to the crystal-field theory... arxiv.org/pdf/cond-mat/0307575*)

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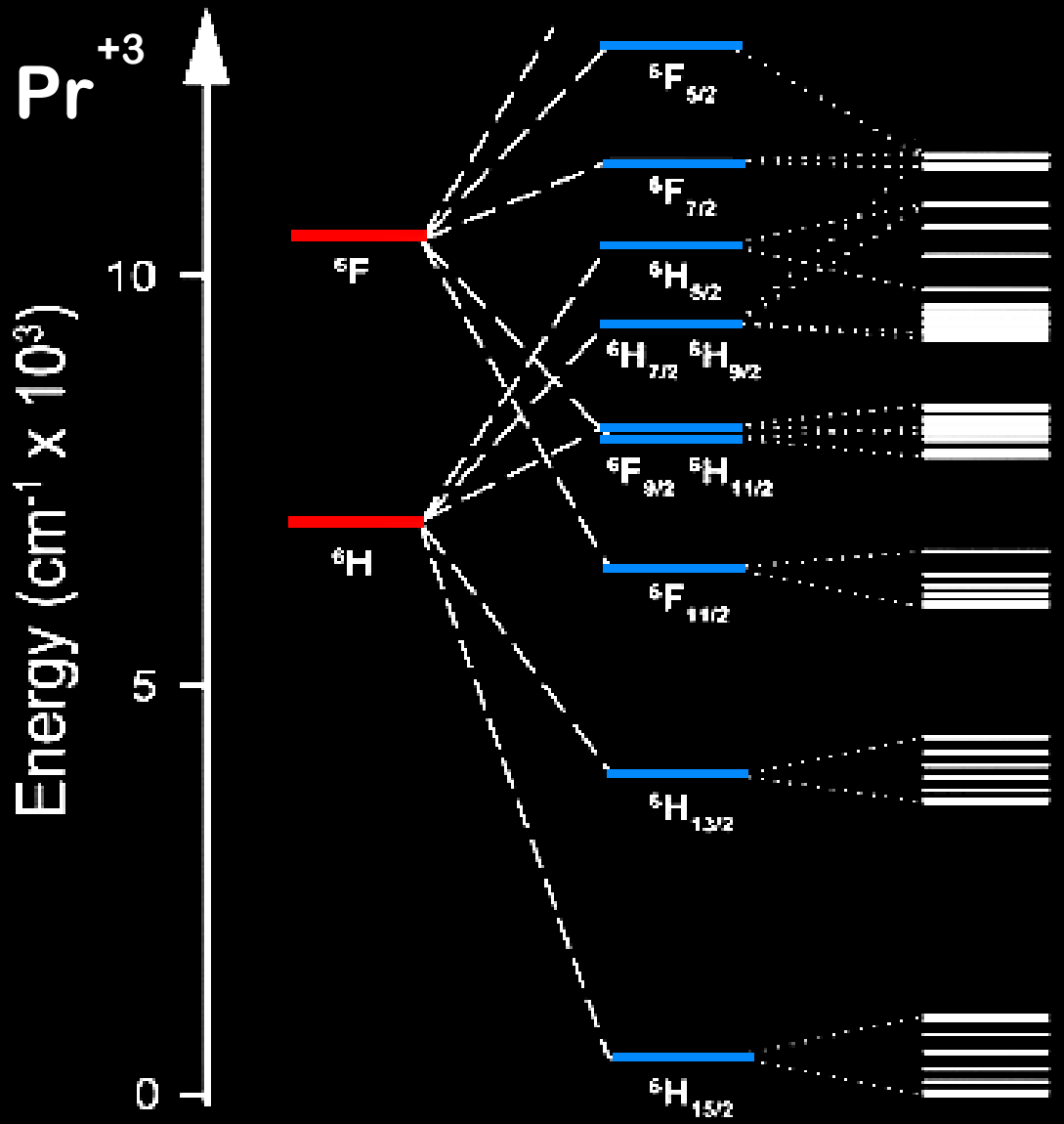
The Fine Electronic Structure
of atoms or ions in crystal



- electronic repulsion
- spin-orbit coupling
- crystal field (CEF) and magnetic interactions

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Hamiltonians

of CEF, spin-orbit and magnetic interactions

base $|\mathbf{L},\mathbf{S},L_z,S_z\rangle$ $\quad \mathbf{H}_{LS} = \mathbf{H}_{CEF} + \mathbf{H}_{S\text{-}O} + \mathbf{H}_{Zeeman} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(\mathrm{L},L_z) + \lambda \mathbf{L}\cdot\mathbf{S} + \mu_B(\mathbf{L} + g_e\mathbf{S})\cdot\mathbf{B}_{ext}$

base $|\mathbf{J},J_z\rangle$ $\quad \mathbf{H}_J = \mathbf{H}_{CEF} + \mathbf{H}_{Zeeman} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(\mathrm{J},J_z) + g_L\mu_B \mathbf{J}\cdot\mathbf{B}_{ext}$

	$L_z=5 S_z=1$	$L_z=5 S_z=0$	$L_z=5 S_z=-1$	$L_z=4 S_z=1$	$L_z=4 S_z=0$	$L_z=4 S_z=-1$	$L_z=3 S_z=1$	$L_z=3 S_z=0$	$L_z=3 S_z=-1$	$L_z=2 S_z=1$	$L_z=2 S_z=0$	$L_z=2 S_z=-1$	$L_z=1 S_z=1$	$L_z=1 S_z=0$
$L_z=5$ $S_z=1$	2.7E+3	0	0	0	0	0	0	0	0	0	0	0	0	0
	-5.942E+2	0	0	0	0	0	0	0	0	0	0	0	-2.19132E+2	0
														0
$L_z=4$ $S_z=1$	0	1.21E+3	0	2.16E+3	0	0	0	0	0	0	0	0	0	0
	0	0	0	1.614E+1	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$L_z=4$ $S_z=0$	0	0	1.21E+3	0	0	0	1.62E+3	0	0	0	0	0	0	0
	0	0	0	0	1.61E+1	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$L_z=4$ $S_z=-1$	0	0	0	0	0	-2.16E+3	0	1.62E+3	0	0	0	0	0	0
	0	0	0	0	0	1.614E+1	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$L_z=3$ $S_z=1$	0	0	0	0	1.62E+3	0	1.62E+3	0	0	0	0	0	0	0
	0	0	0	0	0	0	-5.989E+2	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$L_z=3$ $S_z=0$	0	0	0	0	0	1.62E+3	0	0	0	1.870615E+3	0	0	0	0
	0	0	0	0	0	0	0	-5.99E+2	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	-1.625E+3	0	1.870615E+3	0	0	0

tetragonal D_4 C_{4v} D_{2d} D_4

	sign	value	unit
$B_2^0 =$	-	15.512820	K
$B_4^0 =$	+	0.1152380	K
$B_4^4 =$	+	0.1047619	K
$B_6^0 =$	-	0.0048529	K
$B_6^4 =$	-	0.0181985	K

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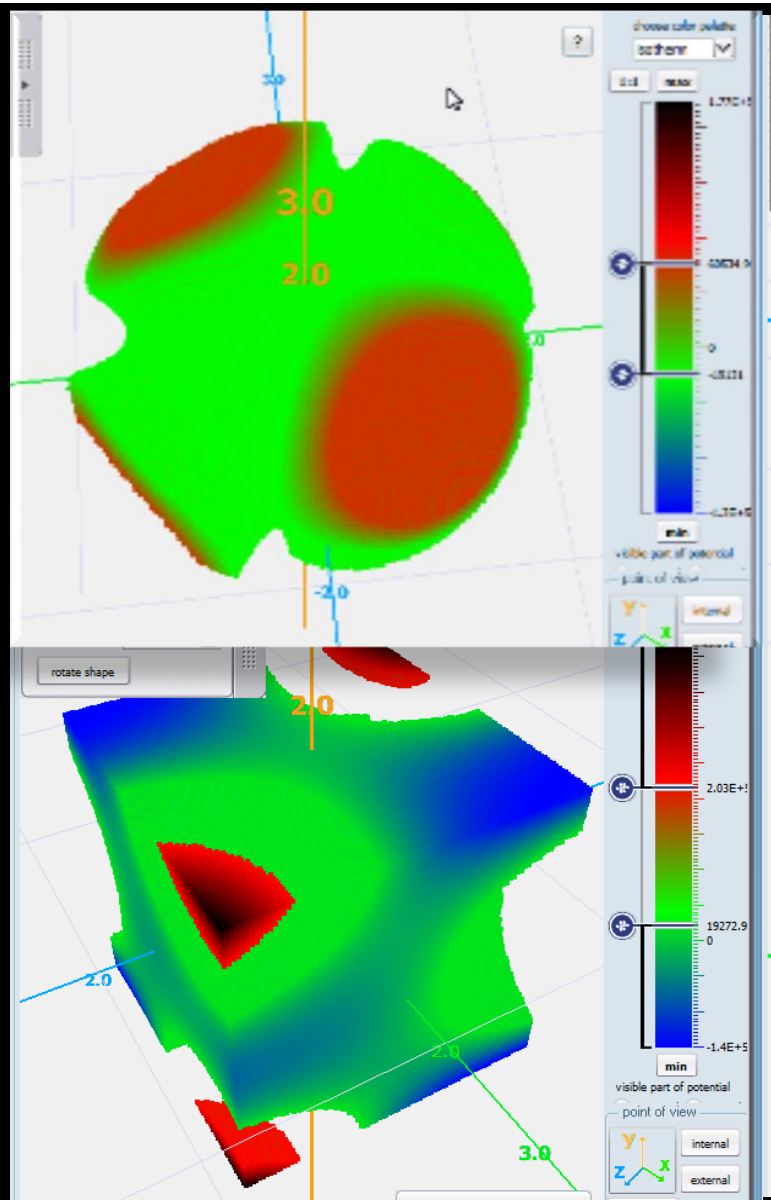
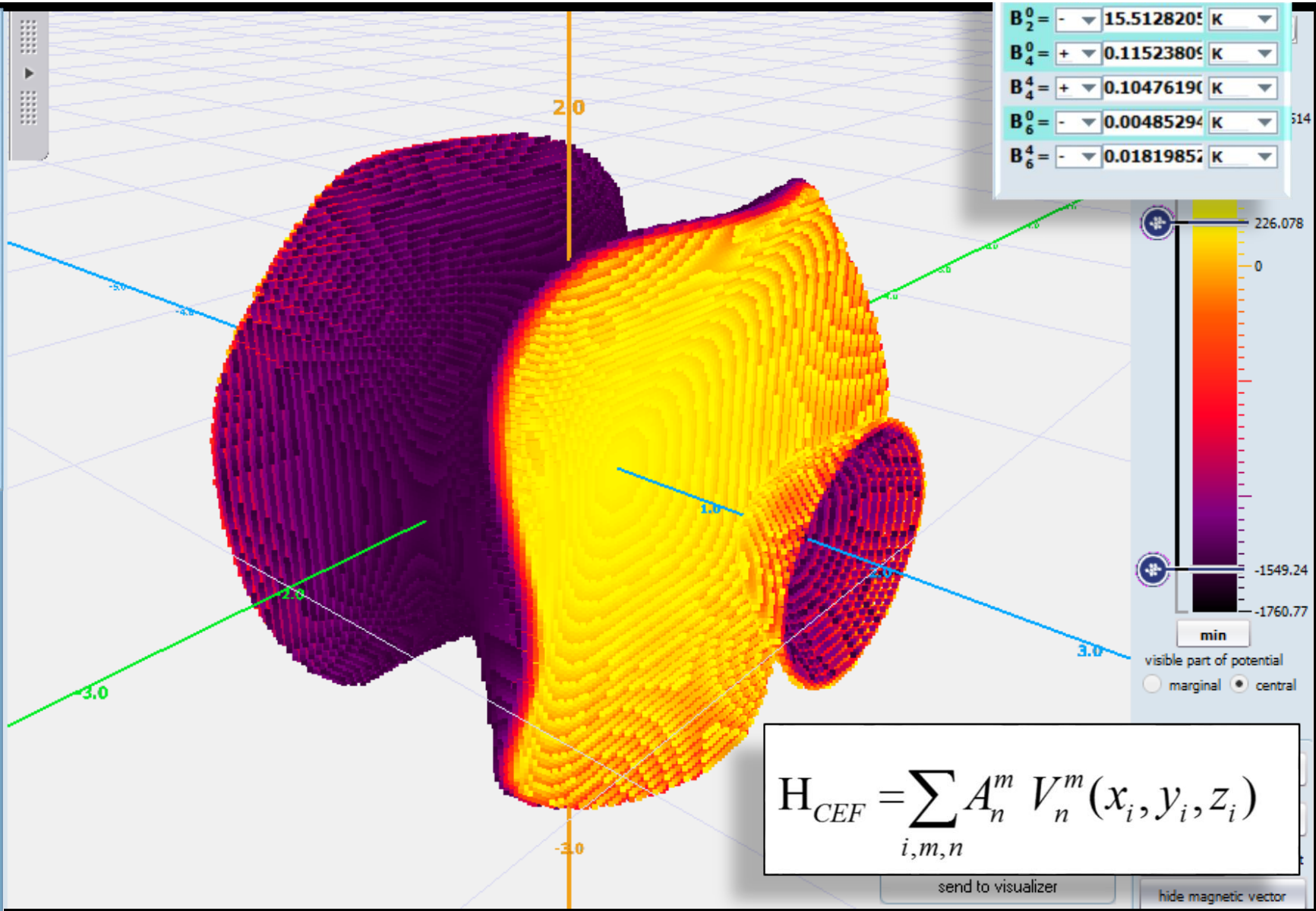
CEF potential Visualization

of Pr^{+3} ion surrounding in crystal of $PrRu_2Si_2$





$$H_{CEF} = \sum_{i,m,n} A_n^m \, V_n^m(x_i, y_i, z_i)$$

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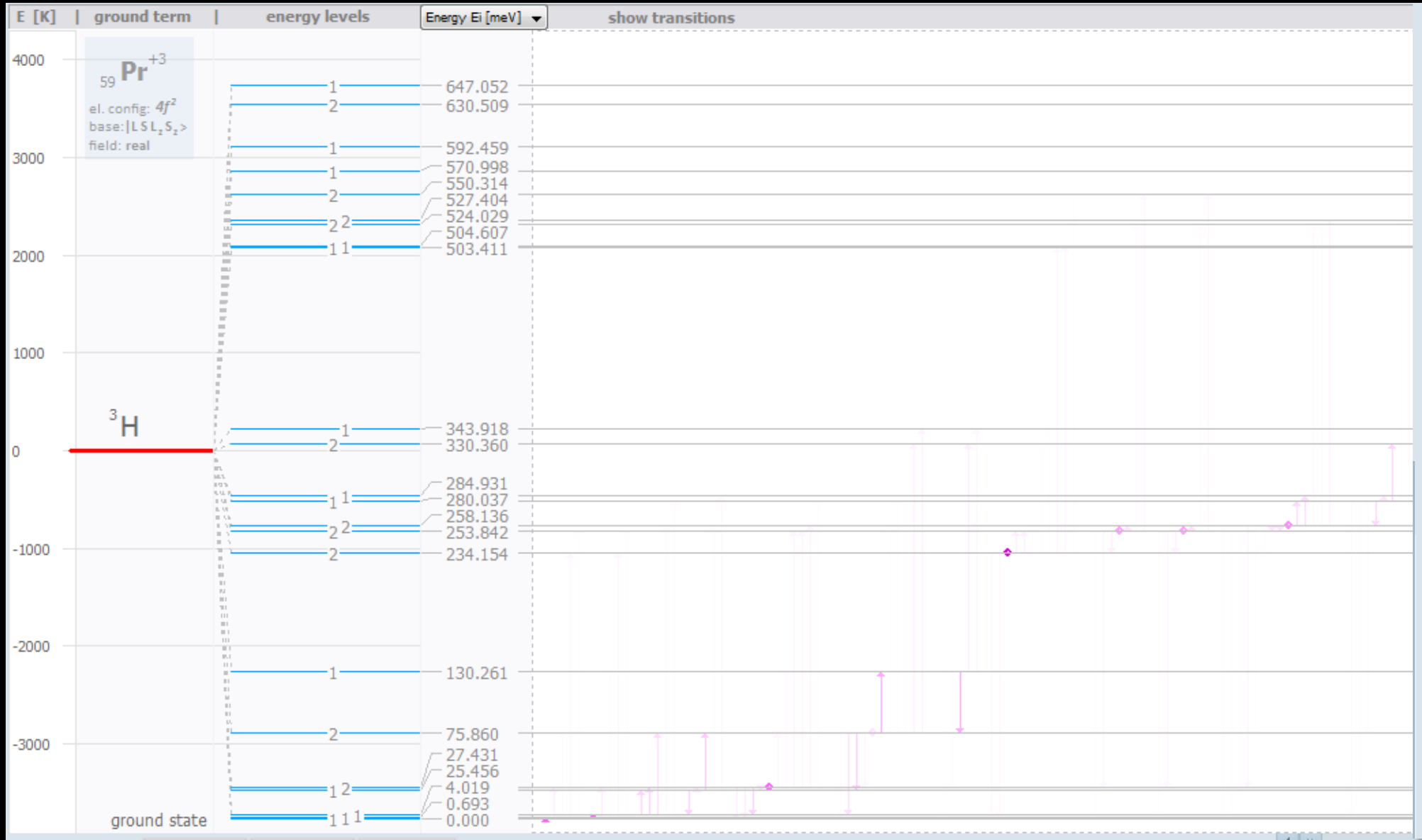
Energy Levels Scheme

of Pr^{+3} ion in $PrRu_2Si_2$ calculated in $|L,S,L_z,S_z>$



0 | +3 | +4

$_{59}Pr^{+3}$

Praseodymium

$[Xe]4f^2$

L=5; S=1; J=4

ground multiplet: $^3H_4$

$\alpha=-2.1\cdot10^{-2}$; $\beta=-7.3\cdot10^{-4}$

$\gamma=6.1\cdot10^{-3}$

tetragonal D_4 C_{4v} D_{2d} D_4

	sign	value	unit
$B_2^0=$	-	15.512820	K
$B_4^0=$	+	0.1152380	K
$B_4^4=$	+	0.1047619	K
$B_6^0=$	-	0.0048529	K
$B_6^4=$	-	0.0181985	K

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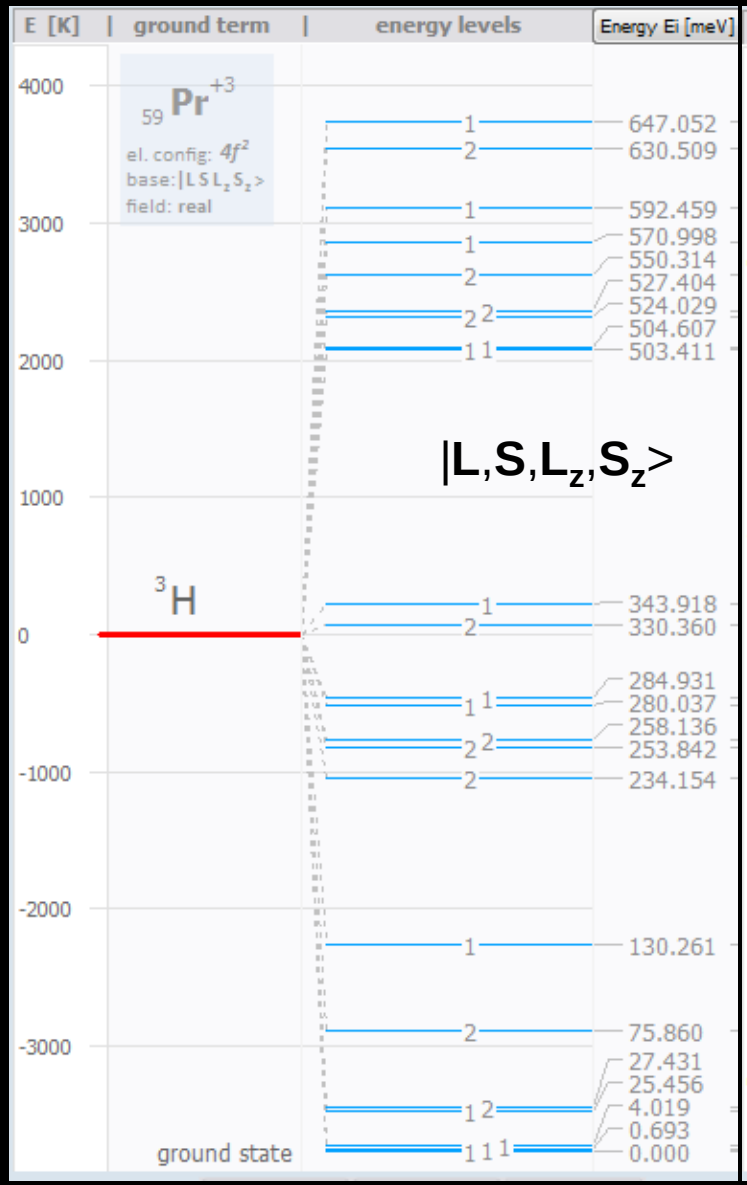
Energy Levels Scheme

of Pr^{+3} ion in $PrRu_2Si_2$ calculated in different bases



0 | +3 | +4

$_{59}Pr^{+3}$

Praseodymium

$[Xe]4f^2$

L=5; S=1; J=4

ground multiplet: $^3H_4$

$\alpha=-2.1\cdot10^{-2}$; $\beta=-7.3\cdot10^{-4}$

$\gamma=6.1\cdot10^{-3}$

tetragonal D_4 C_{4v} D_{2d} D_4

	sign	value	unit
B_2^0 =	-	15.512820	K
B_4^0 =	+	0.1152380	K
B_4^4 =	+	0.1047619	K
B_6^0 =	-	0.0048529	K
B_6^4 =	-	0.0181985	K

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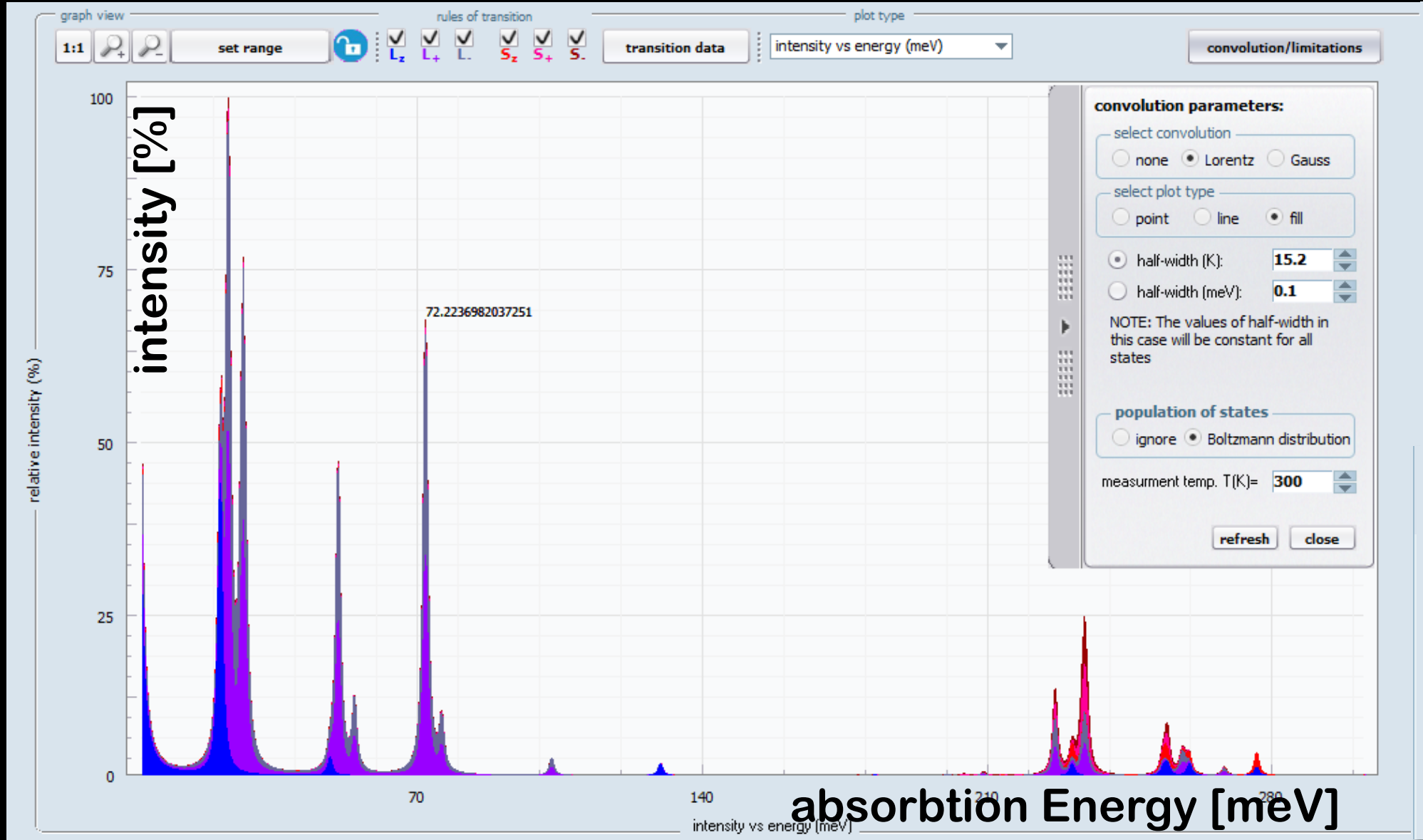
Spectroscopy Simmulation

for Pr^{+3} ion in $PrRu_2Si_2$ - INS simmulated spectrum



0 +3 +4

$_{59}Pr^{+3}$

Praseodymium

$[Xe]4f^2$

L=5; S=1; J=4

ground multiplet: $^3H_4$

$\alpha = -2.1 \cdot 10^{-2}$; $\beta = -7.3 \cdot 10^{-4}$

$\gamma = 6.1 \cdot 10^{-5}$

tetragonal D_4 C_{4v} D_{2d} D_4

	sign	value	unit
B_2^0 =	-	15.512820	K
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B_4^4 =	+	0.1047619	K
B_6^0 =	-	0.0048529	K
B_6^4 =	-	0.0181985	K

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Energy Levels Scheme

of Pr^{+3} ion in $PrRu_2Si_2$ and expected values of $\langle m_i \rangle$

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Thermodynamics
of localized electron systems

Occupation of higher states E_i increases according to Boltzmann statistics

population of states

$$N_i = N \frac{\exp\left(-\frac{E_i}{k_B T}\right)}{Z}$$

statistical sum of states

$$Z(T) = \mathrm{Tr}\left(\exp\left(-\frac{\hat{H}}{k_B T}\right)\right) = \sum_i \exp\left(-\frac{E_i(T)}{k_B T}\right)$$

Helmholtz free Energy

$$F(T) = -k_B T \ln Z(T)$$

Internal Energy

$$U(T) = F(T) - T\left(\frac{\partial F(T)}{\partial T}\right) = -k_B T \frac{\partial}{\partial T}\left(\frac{F(T)}{k_B T}\right)$$

total magnetic moment

$$m_f^{\alpha}(T) = \frac{g_L \mu_B}{Z} \sum_i < J_{\alpha}^{i} > \exp\left(-\frac{E_i(T)}{k_B T}\right)$$

Where: α index - is a directional component, i - numbers the Hamiltonian eigenstates, $<J^i_{\alpha}>$ expected value of the total angular momentum throughout the coating on the α axle in the i-th state.

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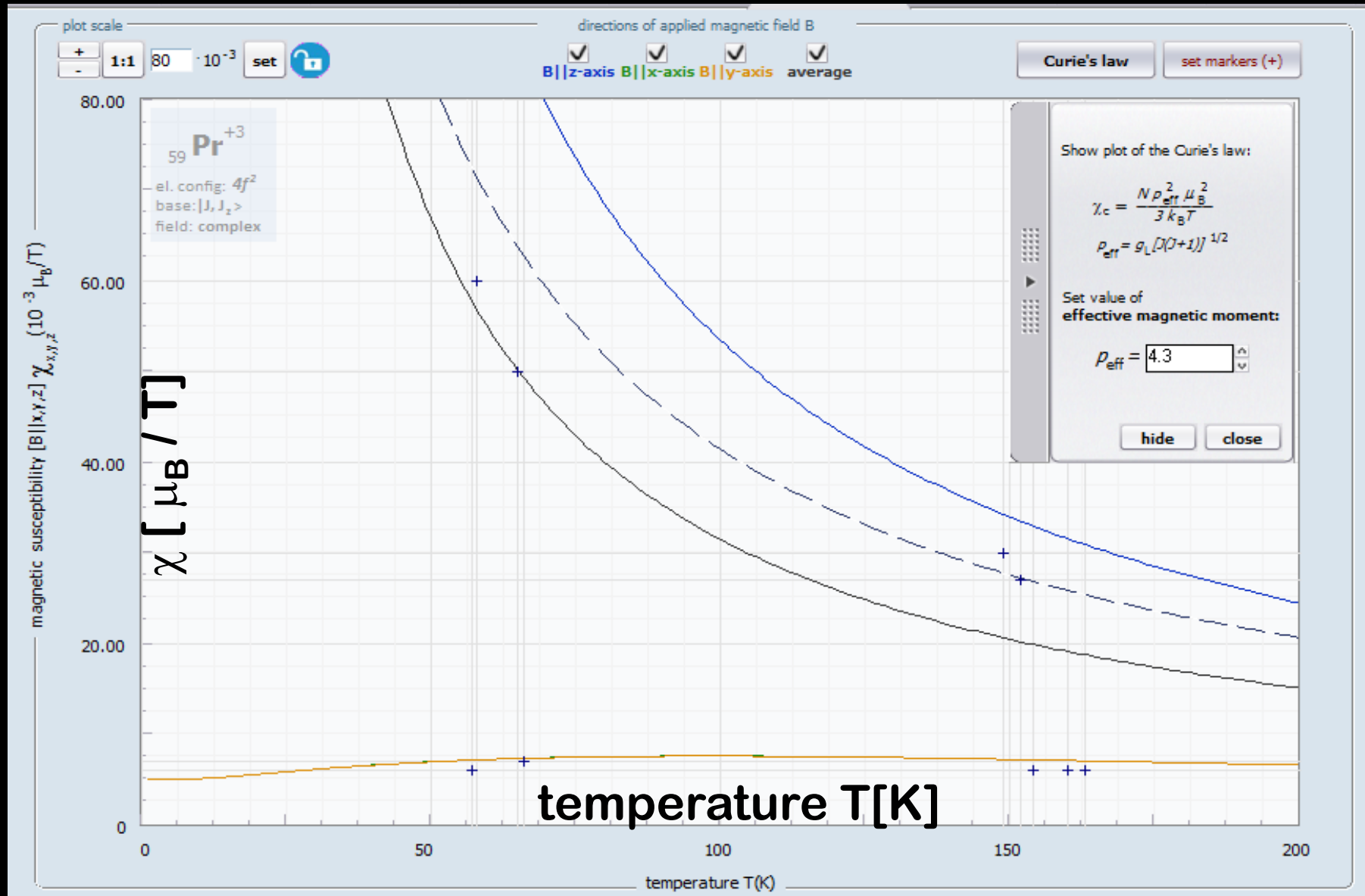
Magnetic susceptibility

simulation for Pr^{+3} ions in $PrRu_2Si_2$ single-crystal



K	μ_B / T
136.0	0
137.0	0
138.0	0
139.0	0
140.0	0
141.0	0
142.0	0
143.0	0
144.0	0
145.0	0
146.0	0
147.0	0
148.0	0
149.0	.03
150.0	0
151.0	0
152.0	0.027
153.0	0
154.0	.006
155.0	0
156.0	0
157.0	0
158.0	0
159.0	0
160.0	.006
161.0	0
162.0	0
163.0	.006
164.0	0
165.0	0
166.0	0
167.0	0
168.0	0

clear

0 | +3 | +4

$^{59}Pr^{+3}$

Praseodymium

$[Xe]4f^2$

L=5; S=1; J=4

ground multiplet: $^3H_4$

$\alpha = -2.1 \cdot 10^{-2}$; $\beta = -7.3 \cdot 10^{-4}$

$\gamma = 6.1 \cdot 10^{-3}$

tetragonal D_4 C_{4v} D_{2d} D_4

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B_4^4 =	+	0.1047619	K
B_6^0 =	-	0.0048529	K
B_6^4 =	-	0.0181985	K

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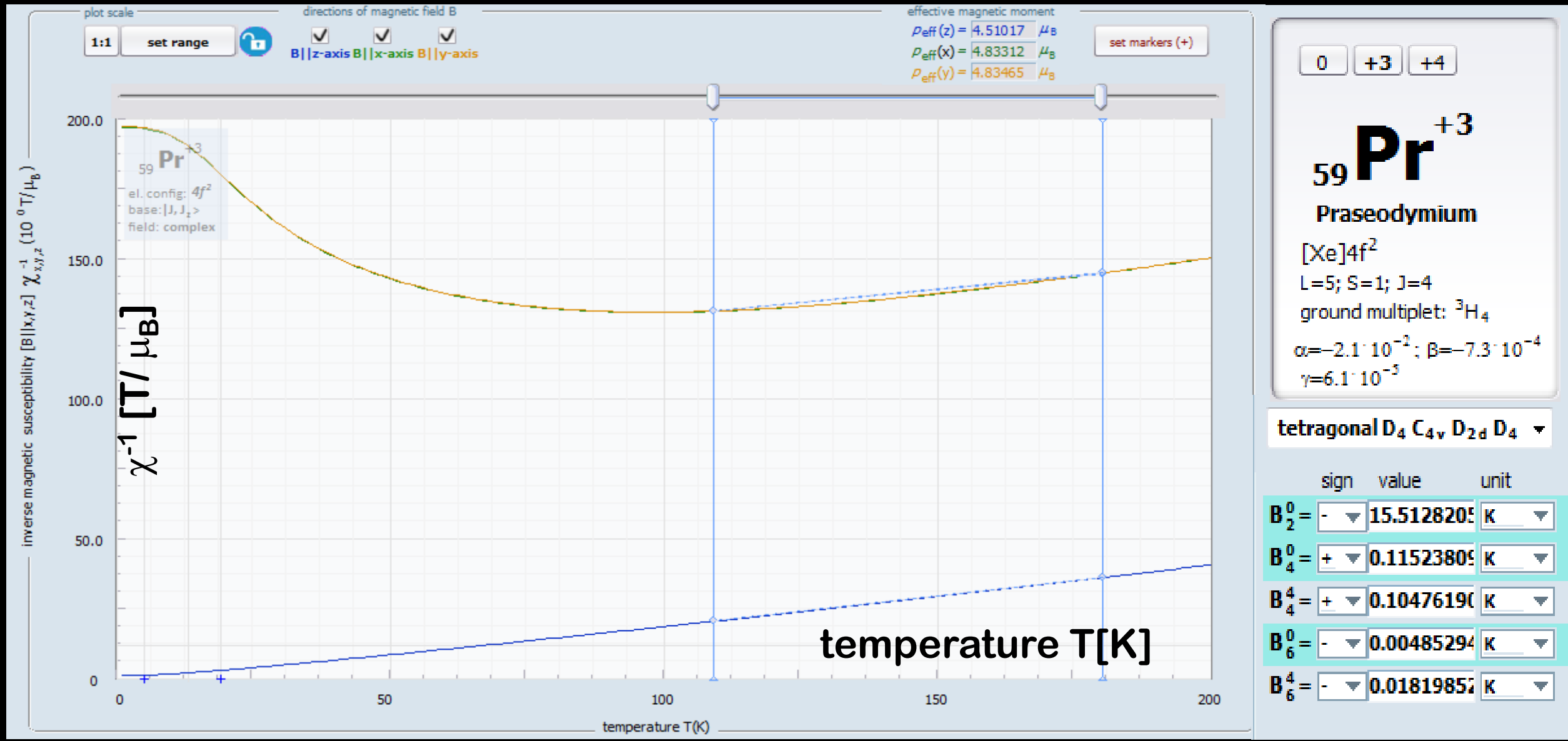
Inverse magnetic susceptibility

simulation for Pr^{+3} ions in $PrRu_2Si_2$ single-crystal



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B_6^0 =	-	0.0048529	K
B_6^4 =	-	0.0181985	K

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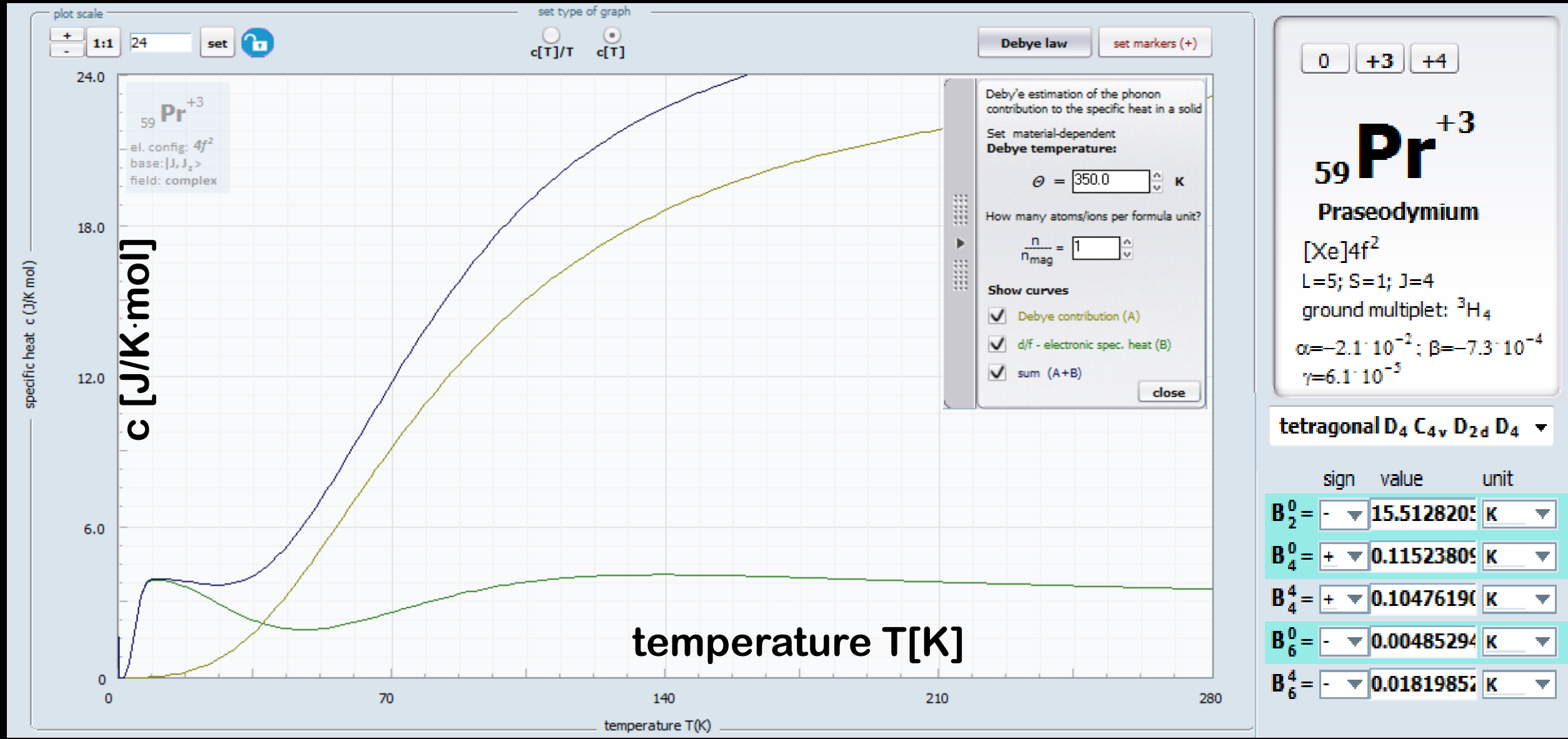
Localized electron specific heat

for Pr^{+3} ions in $PrRu_2Si_2$ and Debye specific heat



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B_6^4 =	-	0.0181985	K

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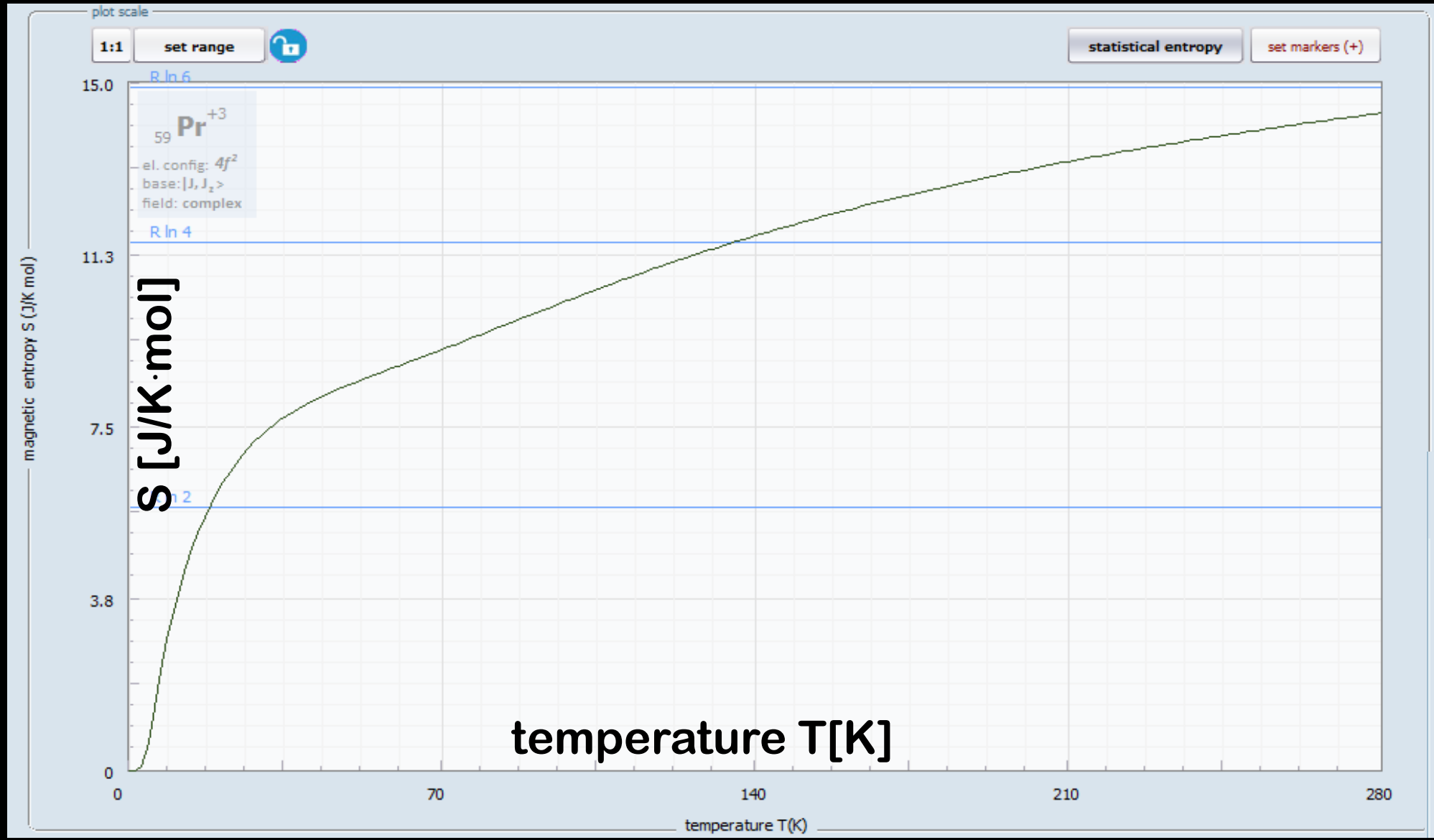
Entropy of $4f^2$ electronic system

of Pr^{+3} ions in $PrRu_2Si_2$



0 +3 +4

$_{59}Pr^{+3}$

Praseodymium

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L=5; S=1; J=4

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$B_6^4=$	-	0.0181985	K

atomic matters
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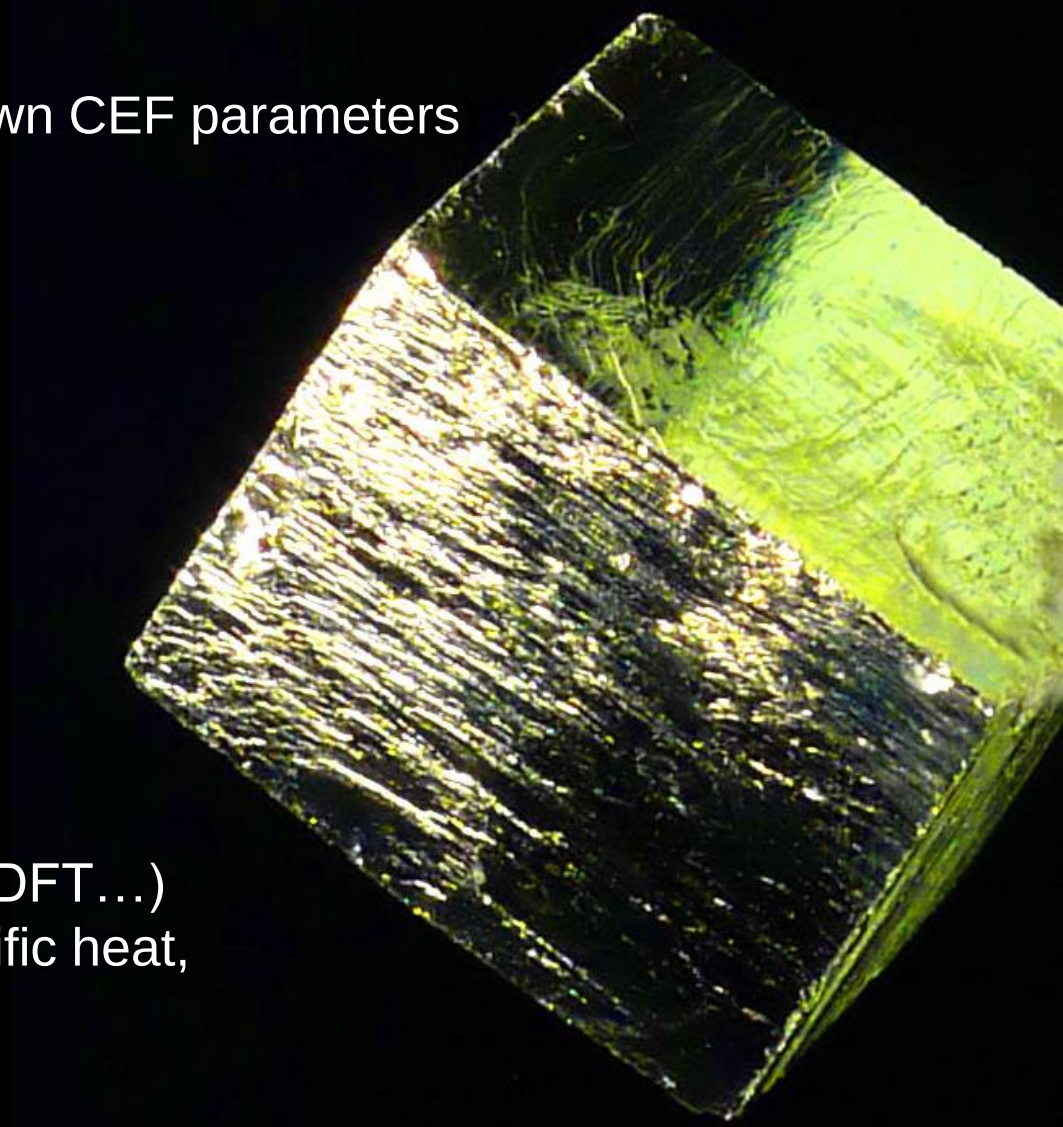
How to find CEF Parameters?

Recalculation from isostructural compounds with known CEF parameters

Point Charge Model CEF parameters estimation

Indirect studies from experimental results:

- Inelastic Neutron Scattering (INS)
- Optic, IR, UV Spectroscopy
- Mössbauer spectroscopy
- X-ray spectroscopy
- Theoretical structure calculation of charge distribution (DFT…)
- Magnetic thermal studies (magnetic susceptibility, specific heat, magnetocrystalline anisotropy…)



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Point Charge Model (PCM) Calculator

periodic table | PCM | potential visualizer

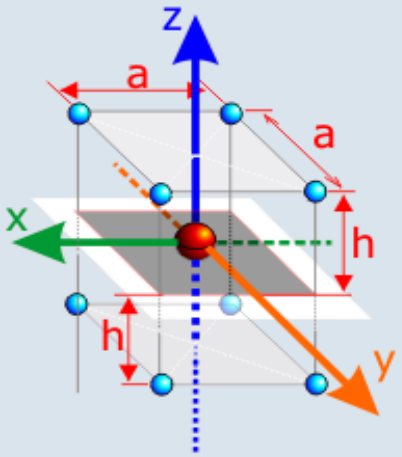
Point Charge Model

Central ion
$3d^4$ Fe^{+4}

coordinating charges
2 e^-

octahedron | tetrahedron | cube | tetragonal | hexagonal | linear

coordination number:**8**
coordination type:
tetragonal



PCM calculated parameters:

B_2^0	330.99212	K
B_4^0	-40.63694	K
B_4^4	-241.32402	K
B_6^0	0	K
B_6^4	0	K

rotate coordinations by 45 degree in xy plane

Input location of point charges

a = 2.02 Å h = 0.94 Å add >>

superposition of potentials

superposition components

square : a = 2.02, h = 0.94
triangle : a = 3, h = 2
point : h = 3

x remove selected potential

clear all

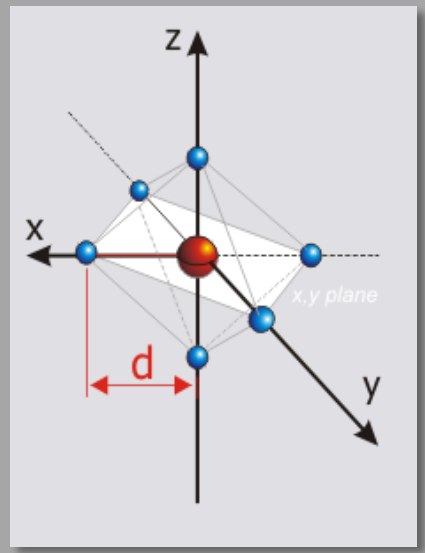
PCM superposition parameters:

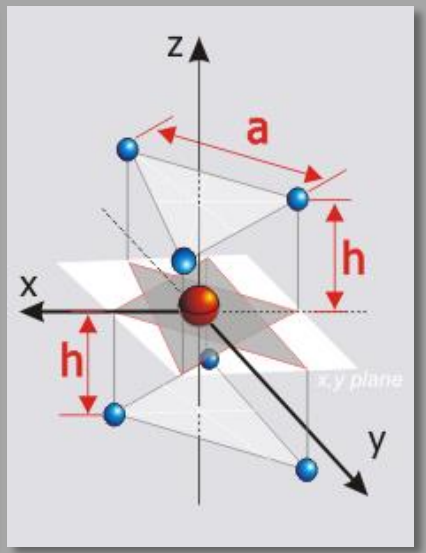
B_2^0	-509.83915	K
B_4^0	-42.18361	K
B_4^3	71.11177	K
B_4^4	-241.32402	K
B_6^0	0	K
B_6^3	0	K
B_6^4	0	K
B_6^6	0	K

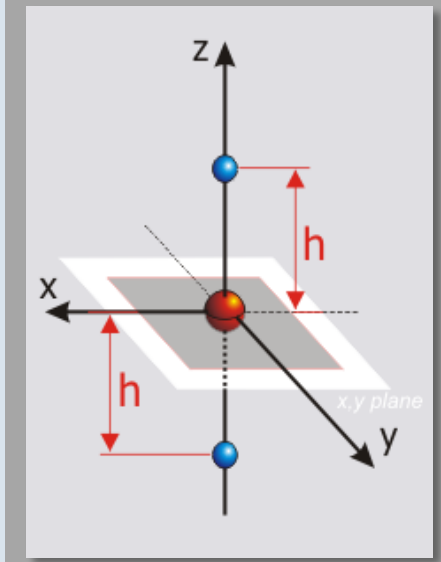
Use these parameters:

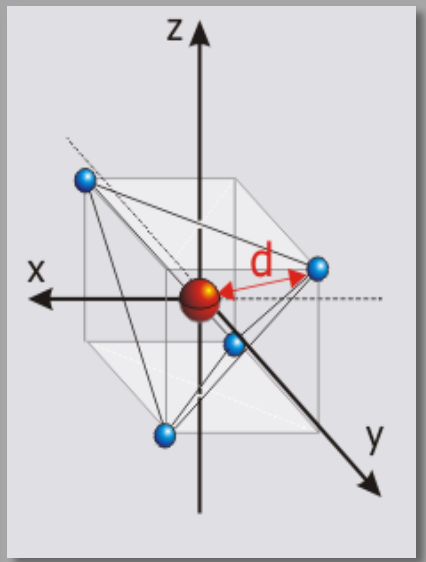
send to calculations

send to visualizer









atomic matters
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CEF recalculation

transformation of CEF parameters between different ions

base $|L,S,L_z,S_z\rangle$ $\mathbf{H}_{LS} = \mathbf{H}_{CEF} + \mathbf{H}_{S\text{-}O} + \mathbf{H}_{Zeeman} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(L,L_z) + \lambda \mathbf{L}\cdot\mathbf{S} + \mu_B(\mathbf{L} + g_e\mathbf{S})\cdot\mathbf{B}_{ext}$

base $|J,J_z\rangle$ $\mathbf{H}_J = \mathbf{H}_{CEF} + \mathbf{H}_{Zeeman} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(J,J_z) + g_L\mu_B \mathbf{J}\cdot\mathbf{B}_{ext}$

$$\mathbf{H}_{CEF} = \sum_{i,m,n} A_n^m V_n^m(x_i,y_i,z_i)$$

$$B_n^m(J,J_z) = \theta_n(J)\langle r_{d,f}^n \rangle A_n^m \qquad B_n^m(L,L_z) = \theta_n(L)\langle r_{d,f}^n \rangle A_n^m$$

$$\theta_2 = \alpha \qquad \theta_4 = \beta \qquad \theta_6 = \gamma$$

Stevens Factors Calculator

Atomic Matters Database

The recalculations of CEF parameters B_n^m are passible in isostructural series according to scheme:

$$B_n^m \rightarrow A_n^m \rightarrow B_n^m$$

known parameters set for defined ion in CEF

set of universal CEF coefficients

new set of CEF parameters for another ion in the same crystal lattice (isostructural compounds)

atomic matters

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Calculation Results

of material properties in paramagnetic satate

- Ag^{2+} ion in **Cs_2AgF_4** [13]
- Ce^{3+} ion in $Ce_2Fe_{14}B$ [14]
- Ce^{3+} ion in CeAs [15]
- Ce^{3+} ion in CeBi [15]
- Ce^{3+} ion in CeFeAsO [26]
- Ce^{3+} in $CeFeAsO_{0.84}F_{0.16}$ [16]
- Ce^{3+} in $CeNi_{0.85}Cu_{0.15}Sn$ [17]
- Ce^{3+} ion in CeP [37]
- Ce^{3+} in $CeRh_{0.8}Pd_{0.2}Sb$ [17]
- Ce^{3+} in $CeRh_{0.9}Pd_{0.1}Sb$ [17]
- Ce^{3+} ion in **$CeRu_2Ge_2$** [18]
- Ce^{3+} ion in $CeRu_2Si_2$ [18]
- Co^{3+} ion **in $LaCoO_3$** [19]
- Cu^{2+} $Cu(C_2H_8N_2)_2Ni(CN)_4$ [20]
- Dy^{3+} ion in Dy_2Fe_{17} [21]
- Dy^{3+} ion in $DyCl_3$ [22]
- Dy^{3+} ion in $DyNi_2$ [21]
- Dy^{3+} ion in $DyNi_5$ [23]
- Dy^{3+} ion in $DyRu_2Si_2$ [24]
- Dy^{3+} ion in ethyl sulfate [25]
- **Dy^{3+}** ion in **$LaCl_3$** [25]
- Dy^{3+} ion in Dy_2Co_{17} [21]
- Er^{3+} ion in **$Er_2Fe_{14}B$** [14]
- Er^{3+} ion in Er_2Fe_{17} [21]
- Er^{3+} ion in $ErAl_2$ [21]
- Er^{3+} in **$ErBa_2Cu_3O_7$** [26]
- Er^{3+} ion in $ErCo_2$ [21]
- Er^{3+} ion in $ErFe_2$ [21]
- Er^{3+} ion in $ErNi_2$ [21]
- Er^{3+} in $ErNi_2B_2C$ [27]
- Er^{3+} ion in **$ErNi_5$** [28]
- Er^{3+} ion in ErNiAl [29]
- Er^{3+} ion in ErP [15]
- Er^{3+} ion in ErRh [15]
- Er^{3+} in $ErRu_2Si_2$ [30]
- Er^{3+} in ethyl sulfate [25]
- Er^{3+} ion in $LaBr_3$ [15]
- Er^{3+} ion in $LaCl_3$ [15]
- Fe^{2+} ion in **$FeBr_2$** [31]
- Ho^{3+} ion in Ho_2Fe_{17} [21}
- Ho^{3+} ion in $HoCo_2$ [21]
- Ho^{3+} ion in $HoFe_2$ [21]
- Ho^{3+} ion in $HoNi_2$ [21]
- Ho^{3+} ion in $HoNi_5$ [23]
- Ho^{3+} ion in HoP [15]
- Ho^{3+} ion in HoRh [15]
- Ho^{3+} in $HoRu_2Si_2$ [24]
- Mn^{3+} i in **$LaMnO_3$** [32]
- Nd^{3+} in **Nd_2Co_{17}** [21]
- Nd^{3+} ion in $NdCl_3$ [25]
- Nd^{3+} ion in $NdCo_2$ [21]
- Nd^{3+} in NdFeAsO [33]
- Nd^{3+} ion in NdN [15]
- Nd^{3+} ion in $NdNi_2$ [21]
- Nd^{3+} in **$Nd_2Fe_{14}B$** [23]
- Nd^{3+} ion in NdP [15]
- Nd^{3+} in $NdRu_2Si_2$ [24]
- Nd^{3+} ion in NdS [15]
- Nd^{3+} ion in NdSe [15]
- Ni^{2+} ion in **NiO** [34]
- Np^{3+} ion in **$NpGa_2$** [35]
- Np^{3+} in **$NpPd_2Al_3$** [36]
- Pr^{3+} in ethyl sulfate [25]
- Pr^{3+} ion in LaB_3 [15]
- **Pr^{3+}** ion in **$LaCl_3$** [25]
- Pr^{3+} ion in PrAg [37]
- Pr^{3+} ion in PrAs [37]
- Pr^{3+} ion in PrBi [37]
- Pr^{3+} ion in **$PrCl_3$** [15]
- Pr^{3+} ion in $PrNi_2$ [21]
- Pr^{3+} ion in $PrNi_2Si_2$ [38]
- Pr^{3+} ion in **$PrNi_5$** [23]
- Pr^{3+} ion in PrS [37]
- Pr^{3+} ion in PrTe [37]
- Pr^{3+} ion in **$PrRu_2Si_2$** [39]
- Sm^{3+} in ethyl sulfate [25]
- Sm^{3+} in $Sm_2Fe_{17}C_{2.6}$ [40]
- Sm^{3+} in $Sm_2Fe_{17}N_3$ [40]
- Sm^{3+} in **$SmBa_2Cu_3O_7$** [41]
- Sm^{3+} ion in $SmNi_5$ [42]
- Tb^{3+} ion in $TbNi_2$ [21]
- Tb^{3+} ion in $TbNi_2Si_2$ [38]
- Tb^{3+} ion in $TbNi_5$ [23]
- Tb^{3+} ion in TbP [15]
- Tb^{3+} ion in $TbPO_4$ [15]
- Tb^{3+} in $TbRu_2Si_2$ [24]
- Tm^{3+} in ethyl sulfate [25]
- Tm^{3+} in $Tm_{25}Y_{75}Al_2$ [15]
- Tm^{3+} in $TmRu_2Si_2$ [45]
- Tm^{3+} ion in TmSb [15]
- U^{3+} ion in **UGa_2** [35]
- U^{3+} ion in **UPd_2Al_3** [46]
- U^{4+} ion in URu_2Si_2 [47]
- Yb^{3+} ion in YbP [15]
- Yb^{3+} in $YbRu_2Si_2$ [45]
- Yb^{3+} in $YbCu_2Si_2$ [48]

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Conclusions

Selected calculations, based on parameters taken from scientific publications [13-45], were performed using ATOMIC MATTERS.

- In all cases the $|L,S,L_z,S_z>$ base is better for precise magnetism calculations and spectra recognition
- The $|J.J_z>$ base is not adequate for some rare earth (RE) ion cases, especially for crystals containing Yb^{3+}, Ce^{3+} and Sm^{3+} ions
- Calculations on complex number matrices always give more precise spectra information. Full, correct directional magnetic information is provided by calculations on complex number matrices only.

Working with atomic matters revealed its usefulness. Visual calculation results, full 3D interactive CEF potential visualization, quickly accessible tools for convention and unit recalculations, and comparison of data graphs from different result sets make the application intuitive and effective.

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Mean Field Approximation
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Atomic matters MFA is a software extension of **atomic matters** for magnetic phase transition simulation according to Mean Field Approximation.

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