Electronic structure and peculiarities of the single-ion magnetic anisotropy of rare-earth ions in the iron oxypnictides *R*FeAsO (R = Ce, Pr, Nd, Sm, Gd)

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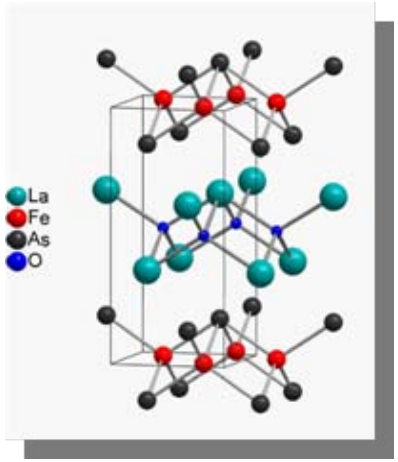
Replacement of La by other rare earth ions leads to increasing of T_c in $RO_{1-x}F_xFeAs$!

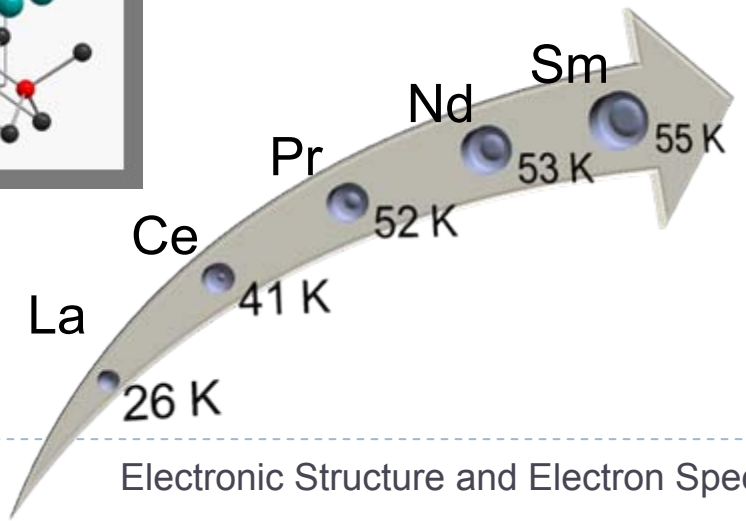
Geometry factor

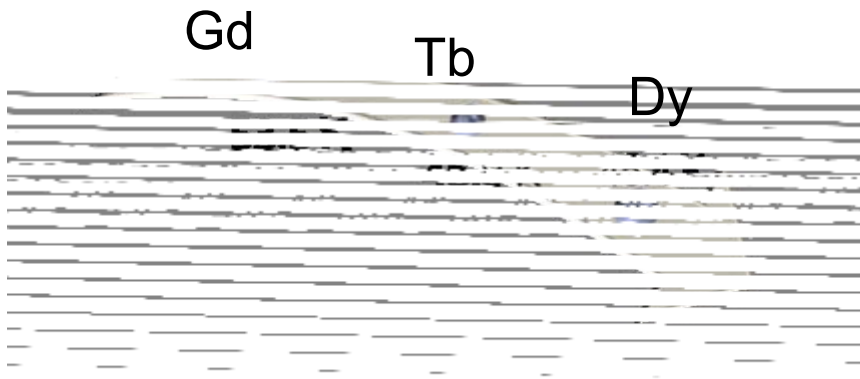
Features of magnetic properties of *R* FeAsO

Magnetic interaction between Fe and *R* subsystems?

Role of magnetic anisotropy of *R*-ions?







The first part of the question has been studied in the work of Maeter with co-authors in 2009.

PHYSICAL REVIEW B **80**, 094524 (2009)

Interplay of rare earth and iron magnetism in *R*FeAsO (*R*=La, Ce, Pr, and Sm): Muon-spin relaxation study and symmetry analysis

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We report zero-field muon spin relaxation (μSR) measurements on *R*FeAsO with *R*=La, Ce, Pr, and Sm. We study the interaction of the FeAs and *R* (rare-earth) electronic systems in the nonsuperconducting magnetically ordered parent compounds of $RFeAsO_{1-x}F_x$ superconductors via a detailed comparison of the local hyperfine fields at the muon site with available Mössbauer spectroscopy and neutron-scattering data. These studies provide microscopic evidence of long-range commensurate magnetic Fe order with the Fe moments not varying by more than 15% within the series *R*FeAsO with *R*=La, Ce, Pr, and Sm. At low temperatures, long-range *R* magnetic order is also observed. Different combined Fe and *R* magnetic structures are proposed for all compounds using the muon site in the crystal structure obtained by electronic potential calculations. Our data point to a strong effect of *R* order on the iron subsystem in the case of different symmetry of Fe and *R* order parameters resulting in a Fe spin reorientation in the *R*-ordered phase in PrFeAsO. Our symmetry analysis proves the absence of collinear Fe-*R* Heisenberg interactions in *R*FeAsO. A strong Fe-Ce coupling due to non-Heisenberg anisotropic exchange is found in CeFeAsO which results in a large staggered Ce magnetization induced by the magnetically ordered Fe sublattice far above T_N^{Ce}. Finally, we argue that the magnetic *R*-Fe interaction is probably not crucial for the observed enhanced superconductivity in $RFeAsO_{1-x}F_x$ with a magnetic *R* ion.

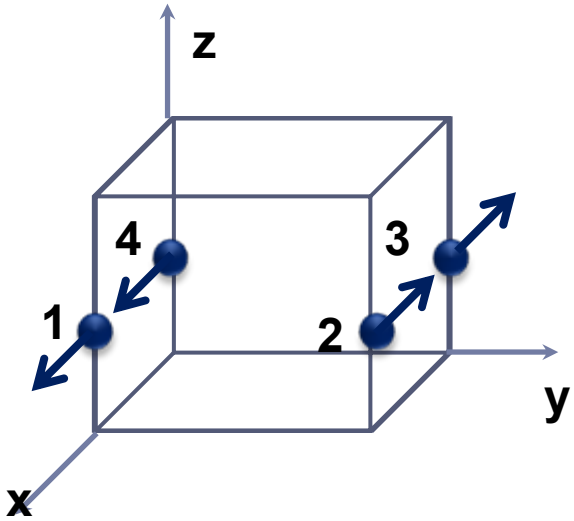
Magnetic interaction between Fe *and R subsystems*

$$H_{ex}^{\mathrm{Fe}-R} = \ldots + J_0^{\mathrm{Fe}-R}\left(\vec{F}^{\mathrm{Fe}} \cdot \vec{F}^{R}\right) + J_1^{\mathrm{Fe}-R}\left(\vec{L}_1^{\mathrm{Fe}} \cdot \vec{L}_1^{R}\right) + \ldots$$

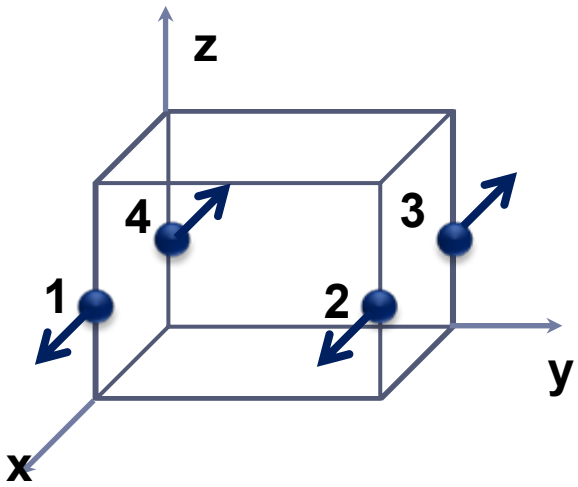
$$H_{an-ex}^{\mathrm{Fe}-R} = \ldots + I_{3xz}^{\mathrm{Fe}-R}\left(L_{3x}^{\mathrm{Fe}} \cdot L_{3z}^{R}\right) + I_{3zx}^{\mathrm{Fe}-R}\left(L_{3z}^{\mathrm{Fe}} \cdot L_{3x}^{R}\right) + \ldots$$

IR	Fe	*R*
τ_1	L_{3y}	0
τ_2	L_{1y}	L_{1z}
τ_3	L_{3z}	L_{3x}
τ_4	L_{1z}	L_{1y}
τ_5	0	L_{3y}
τ_6	0	L_{1x}
τ_7	L_{3x}	L_{3z}
τ_8	L_{1x}	0

$\vec{L}_3 = \vec{m}_1 - \vec{m}_2 - \vec{m}_3 + \vec{m}_4$



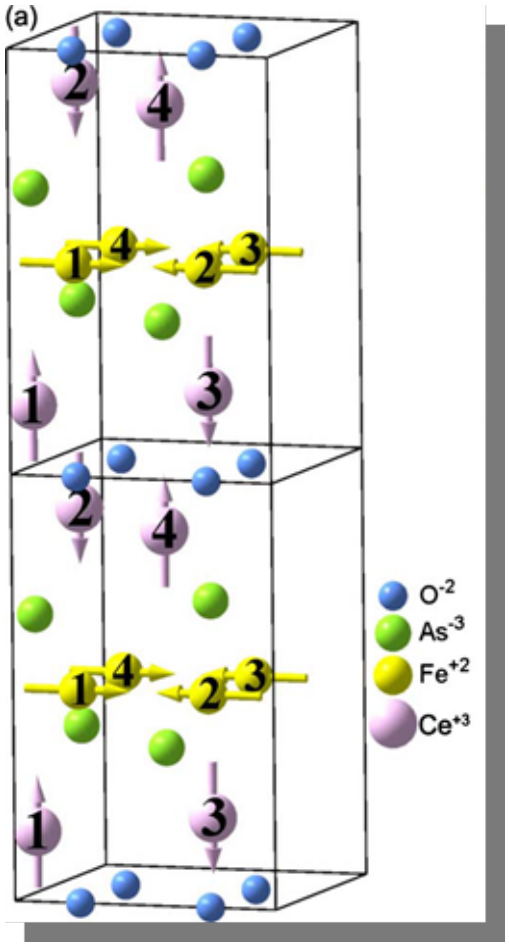
$\vec{L}_1 = \vec{m}_1 + \vec{m}_2 - \vec{m}_3 - \vec{m}_4$



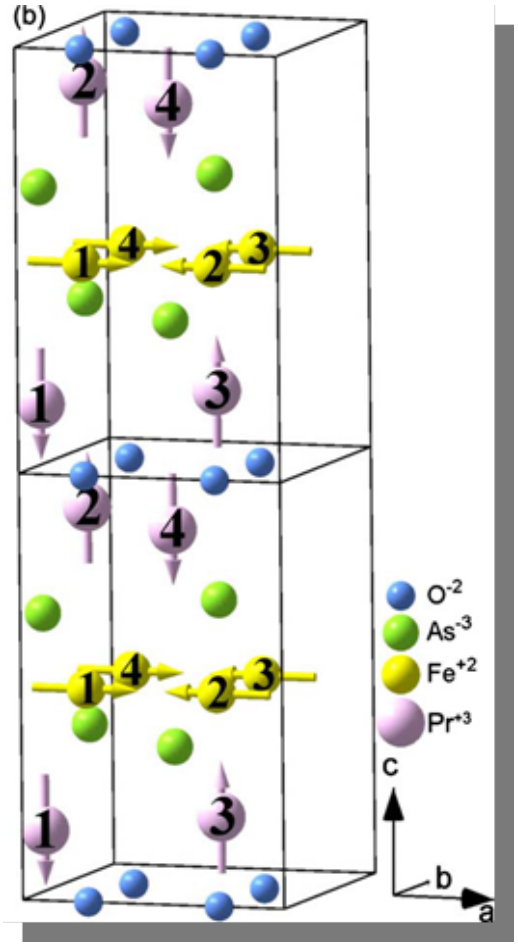
$I_{3xz}(\mathrm{CeFeAsO}) \sim 65.3\ \mathrm{T}/\mu_B$

Direction of the magnetic moments on the R site induced by the L_{3x} Fe order.

CeFeAsO



PrFeAsO



The sign of the coupling constant I_{3xz} Fe-*R is different in the* Ce and the Pr compounds resulting in orientation of the induced moments.

It is known even in SC state the magnetic ordering of *R*-subsystem reserves!

The second part of the problem – the role of magnetic anisotropy of *R*-ions -has been studied in the work of Gornostaeva with co-authors in 2013.

Magnetic properties of Ce^{3+} ion in iron-containing oxypnictide CeFeAsO

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Fiz. Nizk. Temp. **39**, 442–451 (April 2013)

Magnetic properties of a Ce^{3+} ion in two crystallographic phases of a nonsuperconducting oxipnictide CeFeAsO were studied. Ce^{3+}-ion energy levels, *g*-factor values, temperature dependences of magnetic susceptibility components and the forth-order anisotropy constant were calculated within a modified crystal field approach. It was shown that in the tetragonal and orthorhombic phases, the easy direction for the magnetic moment of Ce^{3+} ions corresponds to [110] axis. Comparison of the calculated temperature dependences of susceptibility components to the respective experimental data showed that at temperatures below 100 K, it is necessary to take into account the internal field produced by the magnetic subsystem of iron ions. © *2013 AIP Publishing LLC*
[http://dx.doi.org/10.1063/1.4801990]

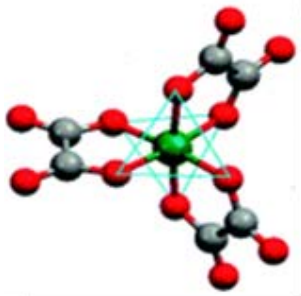
Objective of the work

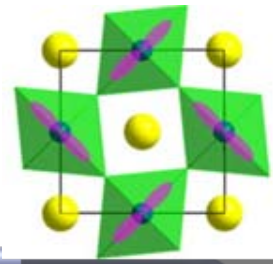
Energy levels of the R^{3+} ions, *g*-factor values, temperature dependences of magnetic susceptibility components and *fourth*-order anisotropy constants have been calculated using the modified crystal field theory (MCFT).

The iron-subsystem effect on the magnetic properties of R^{3+} ions was theoretically studied for both crystallographic phases observed experimentally.

[*] *O. V. Gornostaeva et al., Low Temp. Phys.., **39**, 2013*

Magnetic anisotropy





Single-ion magnetic anisotropy

It is the result of joint interaction of the anisotropic crystal field and spin-orbit interaction.

Manifests itself in the form of an anisotropic dependence the magnetic moment from magnetic field direction

Anisotropy of exchange interaction of an ion pair

It is caused by the spin-orbit interaction between magnetic ions and ligands.

It manifests itself in terms of anisotropic interaction of an ion pair in the spin Hamiltonian.

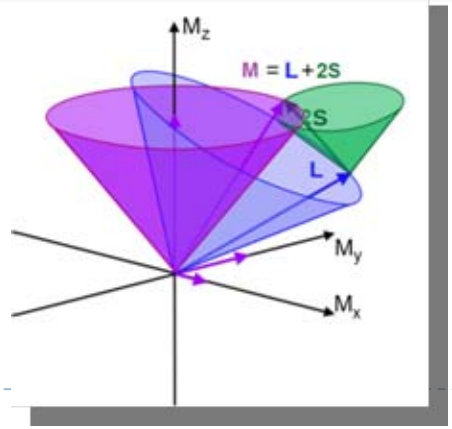
Single-ion magnetic anisotropy

From the standpoint of the nature of the magnetic anisotropy all magnets are divided into two types

Magnets based on $3d$-elements

Magnets based on rare earth $4f$-elements

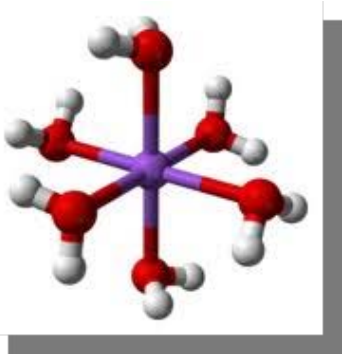
$E_{SO} = \lambda\,(L \cdot S)$



$E_{SO} << E_{CF}$
$\langle L \rangle \approx 0$
$M = g_S \mu_B S$

$E_{SO} >> E_{CF}$
$J = L + S$
$M = g_J \mu_B J$

Effective spin-Hamiltonian for the 3d-ion



Crystal Field Theory

$$H_{ee} >> H_{CF} >> H_{SO} >> H_Z$$

$$\left\{ Z_{eff}^{FI}, q_{eff}, \xi_{nl} \right\} = const$$

M. Pryce, 1950

$$H_{eff} = \left\langle \Gamma, \gamma \middle| H_{SO} + H_Z \middle| \Gamma, \gamma \right\rangle = 2\mu_B \left(\vec{H} \cdot \vec{S} \right) - \sum_{\Gamma', \gamma'} \frac{\left| \left\langle \Gamma', \gamma' \middle| \mu_B \left(\vec{H} \cdot \vec{L} \right) + \lambda \left(\vec{L} \cdot \vec{S} \right) \middle| \Gamma, \gamma \right\rangle \right|^2}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}$$

$$H_{eff} = \sum_{\mu, \nu} \left(\mu_B g_{\mu\nu} H_\mu S_\nu - \lambda^2 \Lambda_{\mu\nu} S_\mu S_\nu - \mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu \right)$$

Single-ion anisotropy

$$g_{\mu\nu} = 2(\delta_{\mu\nu} - \lambda \Lambda_{\mu\nu}),$$
$$\mu, \nu = x, y, z$$

$$\Lambda_{\mu\nu} = \sum_{\Gamma', \gamma'} \frac{\left\langle \Gamma, \gamma \middle| L_\mu \middle| \Gamma', \gamma' \right\rangle \left\langle \Gamma', \gamma' \middle| L_\nu \middle| \Gamma, \gamma \right\rangle}{E_{\Gamma', \gamma'} - E_{\Gamma, \gamma}}$$

Modified Crystal Field Approach (MCFA)

$$H = H_0 + V_{ee} + V_{CF} + V_{SO} + V_H$$

$$V = \sum_{i>j}^{n} \frac{e^2}{r_{ij}} + \sum_{k=1}^{N} \sum_{i=1}^{n} \frac{eq_k}{\left|\vec{r}_i - \vec{R}_k\right|} + \sum_{i=1}^{n} \xi\left(r_i\right)\left(\vec{l}_i, \vec{s}_i\right) + \mu_B \sum_{i=1}^{n} \left(\vec{l}_i + 2\vec{s}_i, \vec{H}\right)$$

$$\left\| V_{\mu\nu} - \varepsilon\delta_{\mu\nu} \right\| = 0, \quad \mu,\nu = 1,\ldots, C^n_{(2l+1)(2s+1)}$$

$$V_{\mu\nu} = \left\langle \Psi\left(\gamma SLM_S M_L\right) | V | \Psi\left(\gamma' SL' M_S M_L{}'\right) \right\rangle$$

$$\Psi\left(SLJM_J\right) = \sum_{\mu} a_\mu \Phi_\mu\left(1, 2, \ldots, n\right)$$

$$\psi\left(nlm_l m_s\right) = R_{nl}(r,\alpha) \cdot Y_{lm}\left(\vartheta,\varphi\right),$$

$$\alpha = Z_{eff} \,/\, n\, a_B$$

*K. V. Lamonova et al., J. Phys. Chem. A. **115**, 13596 (2011).*

*E. S. Zhitlukhina et al., J. Phys.: Condens. Matter. **19**, 156216 (2007).*

MCFA parameters for 3d- and 4f-elements

$$Z_{eff}^{CF} = Z_{eff}^{FI} - \sigma^{CF}$$

$$\xi_{nl} = \xi_{nl}\left(Z_{eff}\right); q_{eff} \neq const$$

3d-elements

$$Z_{eff}^{CF} \neq const$$

$$\xi_{3d} = \xi_{3d}\left(Z_{eff}\right)$$

$$q_{eff} = const$$

$$\xi_{nl} = \frac{\alpha^2}{2} \frac{Z^{2-\beta} Z_{eff}^2}{n^3 l\left(l+1\right)\left(l+1/2\right)}$$

4f-elements

$$Z_{eff}^{CF} = Z_{eff}^{FI}$$

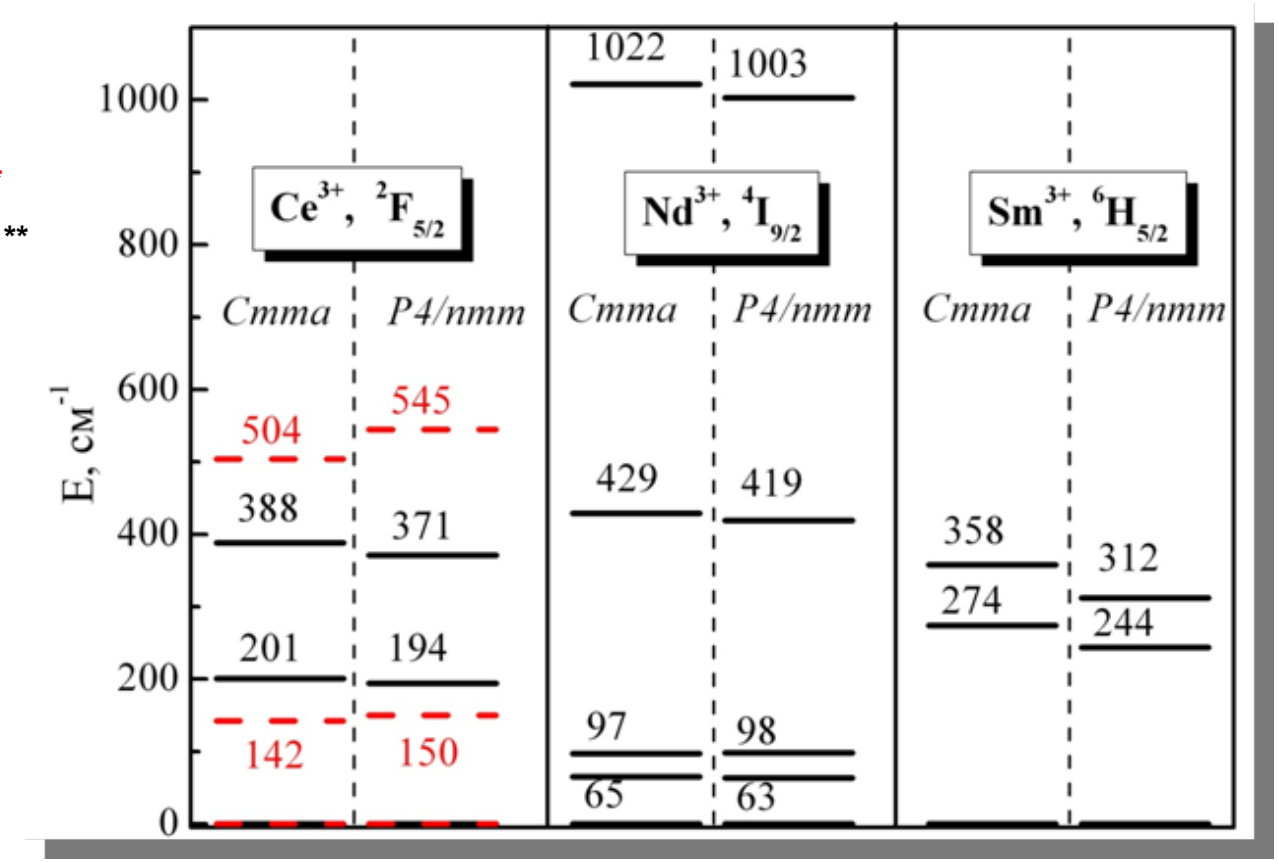
$$\xi_{4f} = const$$

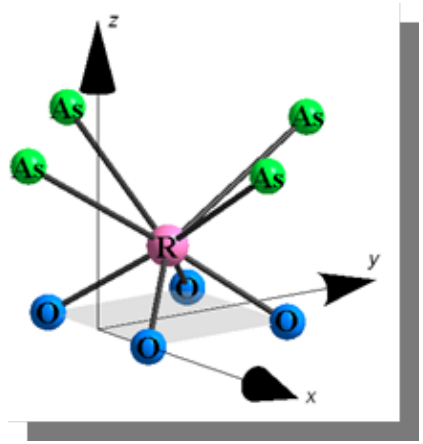
$$q_{eff} \neq const$$

MCFA parameters for Ce^{3+}			
P4/nmm	Z_{eff}^{Ce} = 11.85	q_{eff}^{O} = 0.196	q_{eff}^{As} = 0.294
Cmma	Z_{eff}^{Ce} = 11.85	q_{eff}^{O} = 0.198	q_{eff}^{As} = 0.297

Experimental and calculated crystal levels of R^{3+}-ions in $[RO_4As_4]$-coordination complex

Exp.*
Calc.**

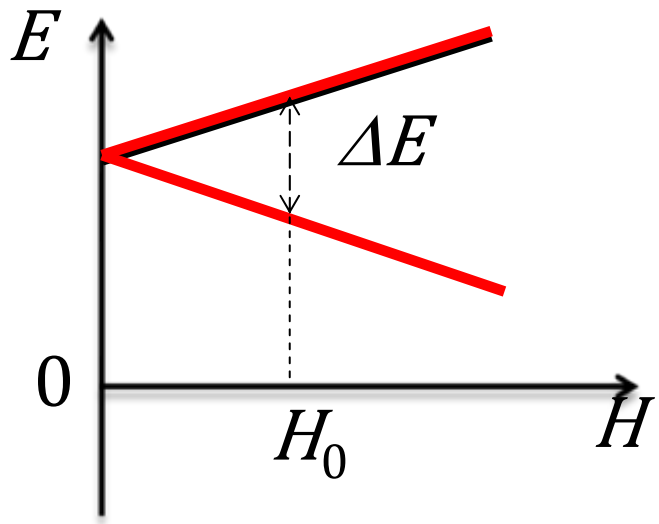


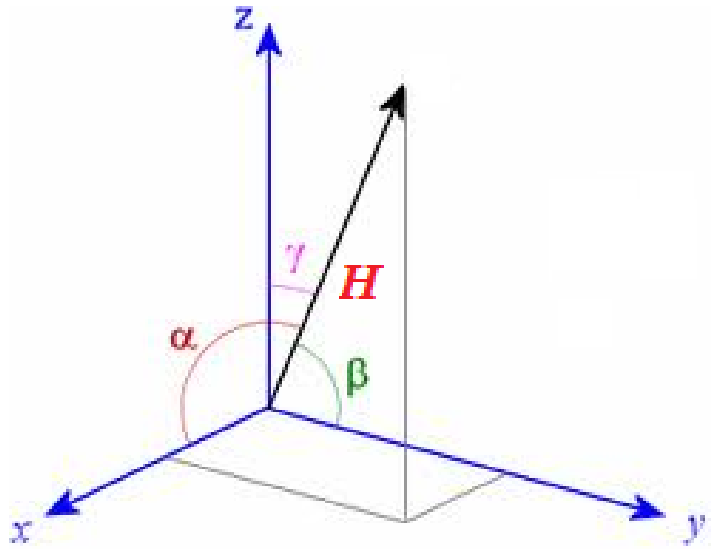


*S. Chi, *et al*, PRL **101**, 21702 (2008).

**O. V. Gornostaeva et al FNT 2013

Calculation of g-factors and reconstruction of g-tensor components





$$g(\alpha,\beta,\gamma)=\frac{\Delta E}{\mu_B \Delta H(\alpha,\beta,\gamma)}$$

$$\vec{\xi}=(\cos\alpha,\cos\beta,\cos\gamma)$$

$$g_{(\alpha\beta\gamma)}=\frac{\vec{\mu}\cdot\vec{H}}{\mu_B\cdot|\vec{H}|}=\frac{\mu_B\cdot|\hat{g}\vec{J}|\cdot|\vec{H}|}{\mu_B\cdot|\vec{H}|}=|\hat{g}\vec{J}|=|\hat{g}\vec{\xi}^{\,T}|$$

g-factors and g-tensors calculated by MCFA and CFT

MCFA

g-tensors for the lowest doublet of Ce^{3+} in two phases	
Cmma	***P4/nmm***
$\begin{bmatrix} 2.618 & 0 & 0 \\ 0 & 2.490 & 0 \\ 0 & 0 & 0.887 \end{bmatrix}$	$\begin{bmatrix} 2.555 & 0 & 0 \\ 0 & 2.555 & 0 \\ 0 & 0 & 0.887 \end{bmatrix}$

CFT ***P4/nmm***

$$g_{\perp} = g_J \left\langle \psi^{\downarrow}_{(\mathrm{I})} \middle| J^{+} \middle| \psi^{\uparrow}_{(\mathrm{I})} \right\rangle = 2{,}571;$$

$$g_{\parallel} = 2 g_J \left\langle \psi^{\uparrow}_{(\mathrm{I})} \middle| J_z \middle| \psi^{\uparrow}_{(\mathrm{I})} \right\rangle = 0{,}857\,.$$

Anisotropy of Kramers ion

To determine the anisotropy of the Kramers ion we should:

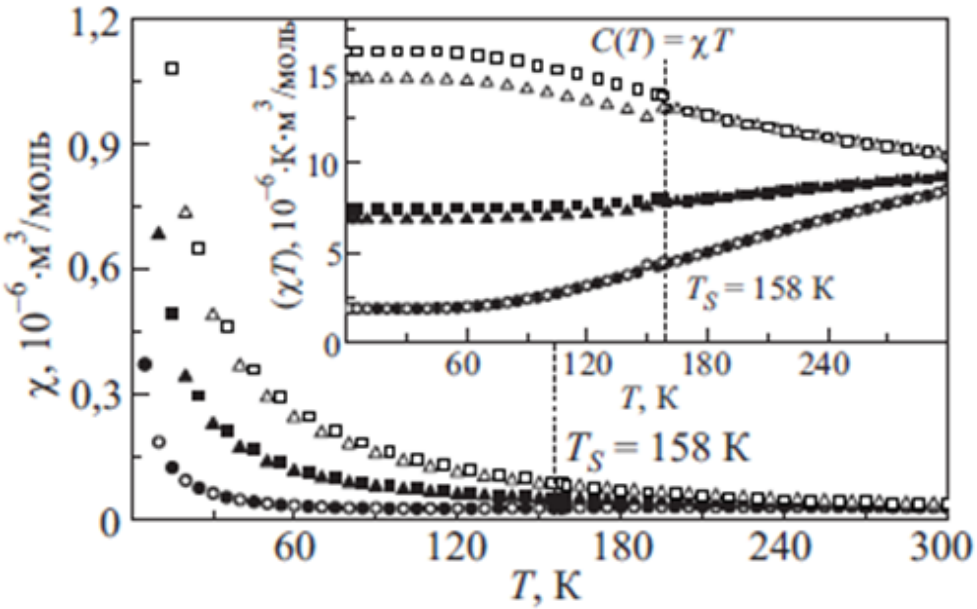
1. to measure (calculate) the g-factor values at least for 6 crystallographic directions;
2. to reconstruct the g-tensor components and to diagonalize the g-tensor;
3. the largest component of the diagonalized g-tensor together with the eigenvector of g-tensor indicate “easy direction” of the magnetic moment.

This direction is determined by the site crystallographic symmetry of paramagnetic ion.

The temperature dependence of the Ce^{3+} magnetic susceptibility

$$\chi_{\sigma\rho} = \frac{\mu_B^2}{k} \cdot \frac{C(T)}{T}$$

$$C_{\sigma\rho}(T) = \sum_{i=1}^{N} g^2_{(i)\sigma\rho} \exp\left(-\frac{\varepsilon_{(i)\sigma\rho}}{kT}\right) \Bigg/ \sum_{i=1}^{N} \exp\left(-\frac{\varepsilon_{(i)\sigma\rho}}{kT}\right)$$



$$\mu_0 \cdot H_{ex} = 5 \text{ T}$$

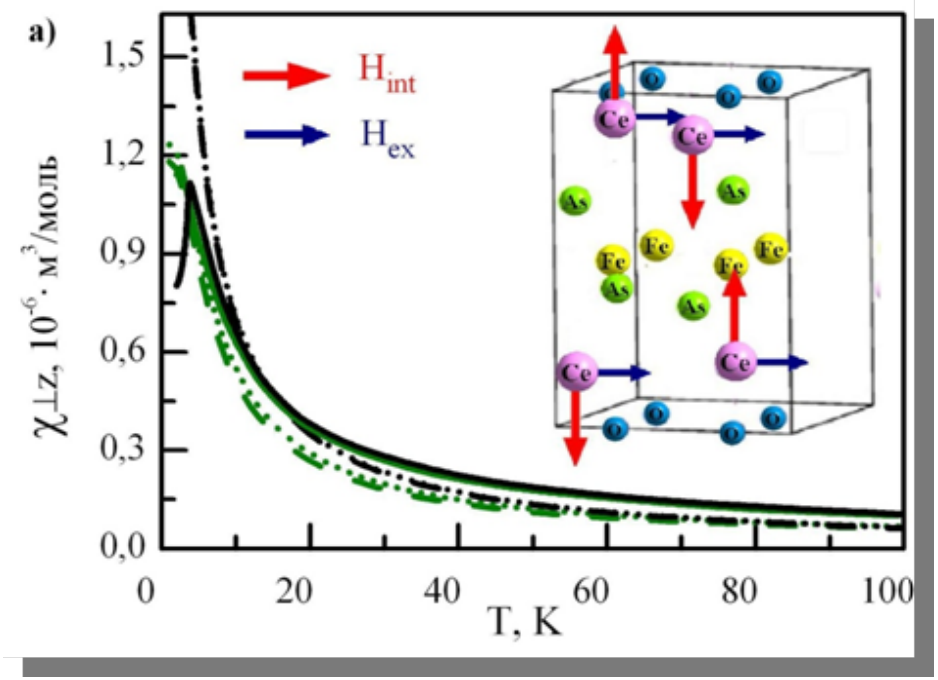
:■, □ - χ_x

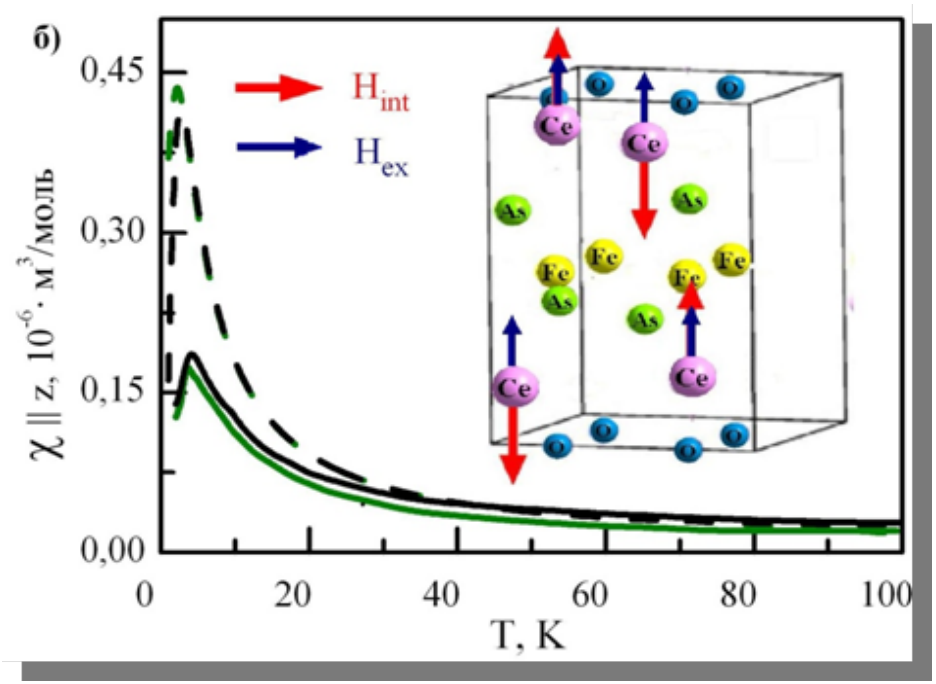
▲, Δ - χ_y

●, ○ - χ_z

Black symb. – $\mu_0 \cdot H_{int} = 0$ T
White symb. - $\mu_0 \cdot H_{int} \neq 0$ T

Experimental and calculated dependences of magnetic susceptibility for CeFeAsO





$\mu_0 \cdot H_{ex} = 1$ T (exp.*)

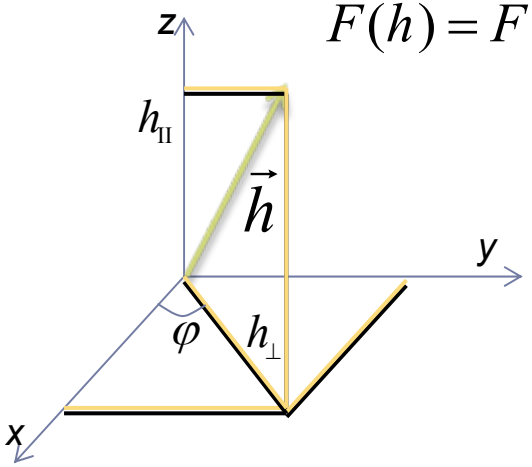
$\mu_0 \cdot H_{ex} = 5$ T (exp.*)

$\mu_0 \cdot H_{ex} = 1$ T (calc.)

$\mu_0 \cdot H_{ex} = 5$ T (calc.)

*A. Jesche *et al.*, *New Journal of Physics* **11** 10305 (2009).

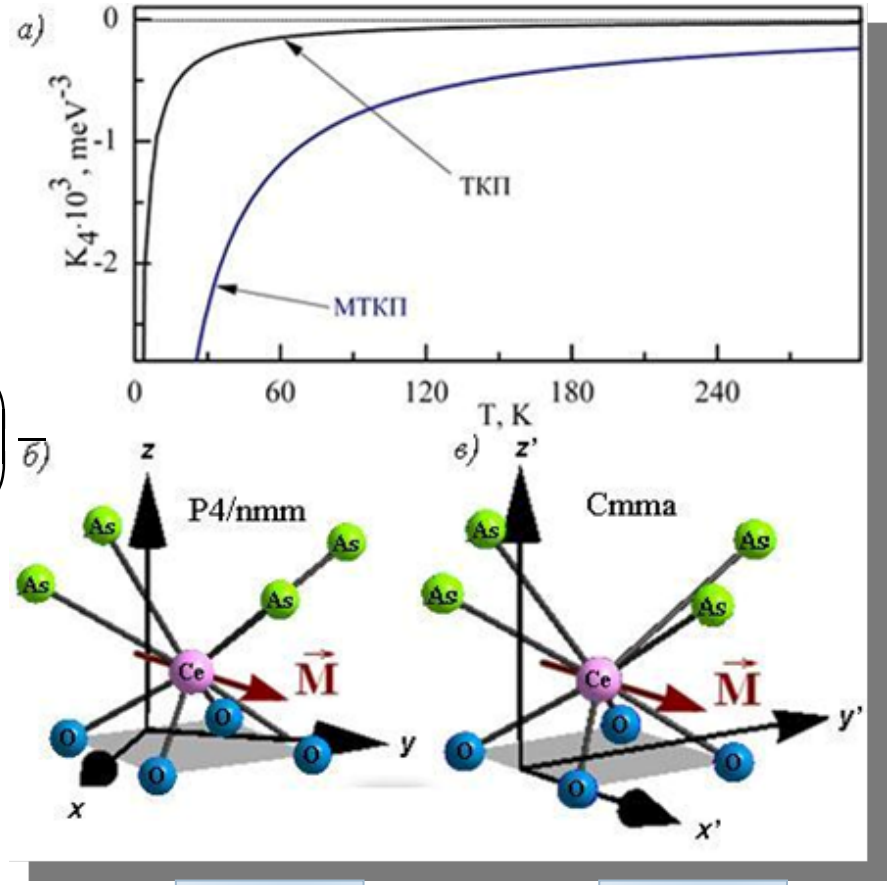
Fourth-order of anisotropy constant



$$F(\vec{h}) = F(0) - \frac{1}{2}\chi_{II} h_z^2 - \frac{1}{2}\chi_\perp h_\perp^2 + \alpha_4 (h_x^4 + h_y^4) + \beta_4 h_z^4 + \gamma_4 h_x^2 h_y^2 + \delta_4 h_\perp^2 h_z^2$$

$$F(h) = F_0(h^2) + \frac{1}{2g_J}(\chi_\perp - \chi_\parallel)\left(h_z^2 - \frac{1}{3}h^2\right) - K_4 \cdot (h_x^4 + h_y^4 - 6h_x^2 h_y^2) + \ldots$$

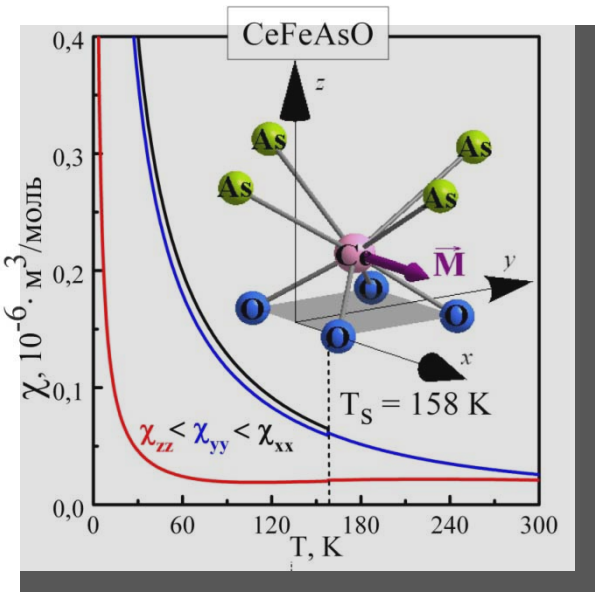
$$K_4 = (\gamma_4 - 2\alpha_4)/8$$

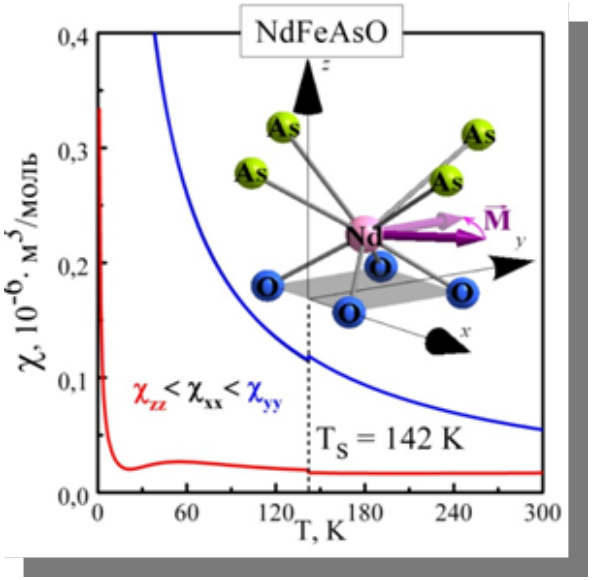


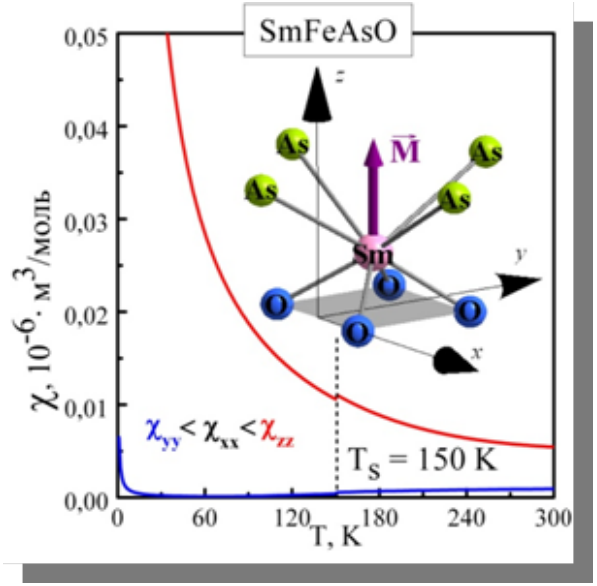
<110> <110>

Magnetic moment direction in tetraphase coincides with one in orthophase!

Temperature dependence of R^{3+} susceptibility components







Ce^{3+}: *in the both phases the "easy direction" is* [110] *axis*

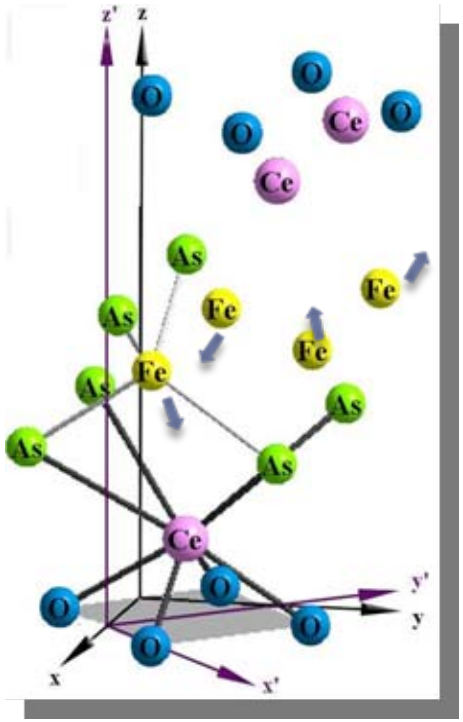
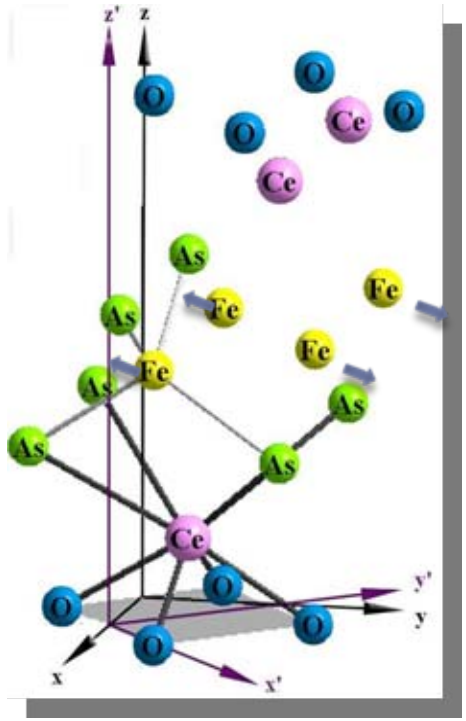
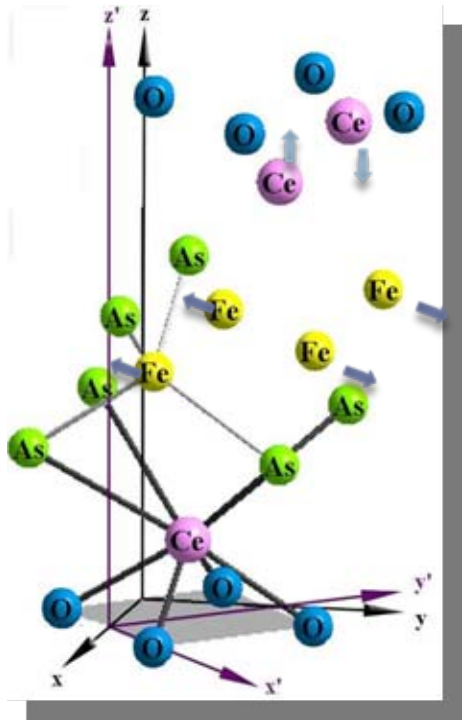
Nd^{3+}: *in tetraphase the "easy direction" is* [010] *axis*

in orthphase the "easy direction" is [110] axis

Sm^{3+}: *in the both phases the "easy direction" is* [100] *axis*

Conclusions

- We propose new approach - modified crystal field theory - to calculate the magnetic properties of rare-earth ions. This approach allows to calculate the energy levels of 3d- and 4f-ions in arbitrary crystal environment with accounting of spin-orbit interaction.
- We show that the rare earth ions in the crystal-environment with 1111-symmetry always remain in highly anisotropic magnetic state.
- If this anisotropy is “easy plane” one than the R magnetic fluctuations always induce the Fe magnetic fluctuations, which are perpendicular to the plane
- One should stress that the iron magnetic subsystem has easy plane anisotropy. Accordingly, the easy plane Fe magnetic fluctuations will produce the rare-earth magnetic fluctuations along hard axis.
- We conclude that due to interplay between iron and rare earth subsystems in the R111 compounds the magnetic fluctuations of iron subsystems even in the doped nonmagnetic case never been isotropic.

Structural and magnetic transitions in CeFeAsO

	T_S = 158 K		T_N (Fe) = 140 K		T_N (Ce) = 4.4 K	
PM	→	PM	→	AFM	→	AFM
P4/ nmm		Cmma		Cmma		Cmma