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РЕЗОНАНСНОЕ РАССЕЯНИЕ СИНХРОТРОННОГО ИЗЛУЧЕНИЯ

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План

- 1) Простые результаты, получающиеся в диполь-дипольном приближении в теории рассеяния.
- 2) Магнитное рассеяние рентгеновских лучей, резонансное и нерезонансное, ставшее в последние годы рабочим методом исследования магнетиков конкурирующим с дифракцией нейтронов.
- 3) Тепловые движения атомов постоянно меняют симметрию атомного окружения и вызывают появление дополнительной переменной анизотропии рентгеновской амплитуды рассеяния.
- 4) Резонансная дифракция является уникальным методом изучения диполь-квадрупольного и квадруполь-квадрупольного вкладов в частности, киральности.
- 5) Интерференция магнитных и немагнитных вкладов в резонансное рассеяние позволяет измерить знак взаимодействия Дзялошинского-Мория в магнетиках

Рентгеновская спектроскопия поглощения

Methods

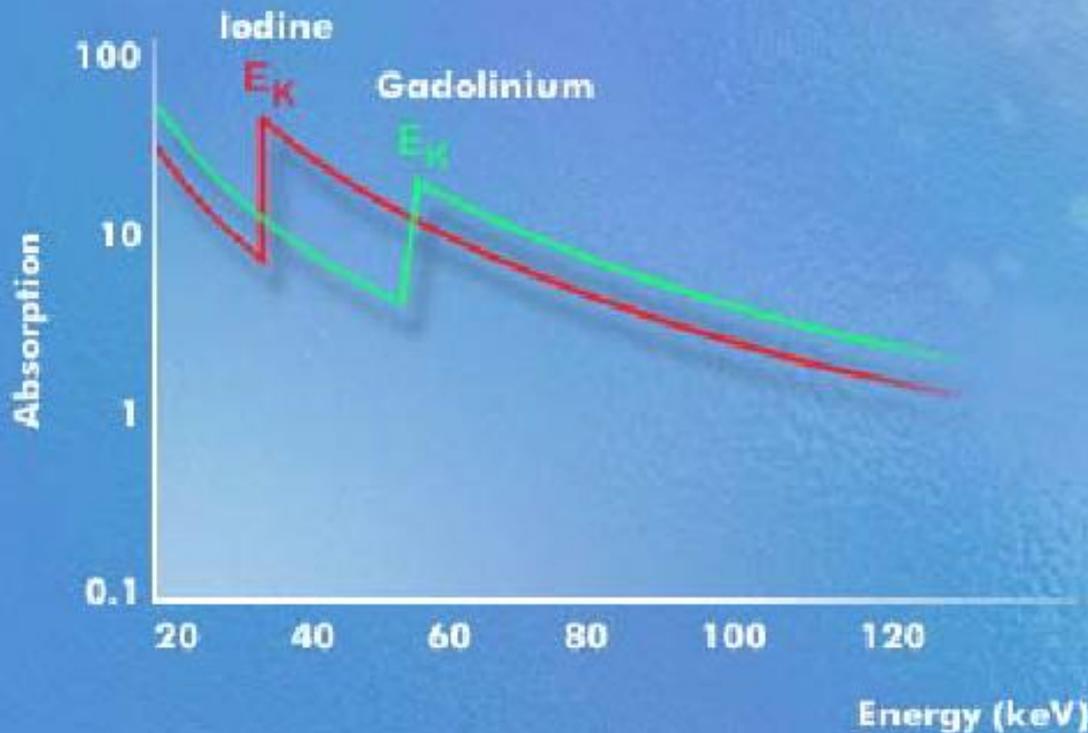
X-ray absorption spectroscopy

X-ray absorption spectroscopy

Absorption edges

The absorption edges observed in an absorption spectrum are characteristic of the successive electron shells in an atom and are one of the signatures of the chemical element being probed. With a beam of photons of a well-defined energy, electrons can be ejected from the innermost shells and, in such a way, certain atoms of a material can be selectively **excited** or **ionized**.

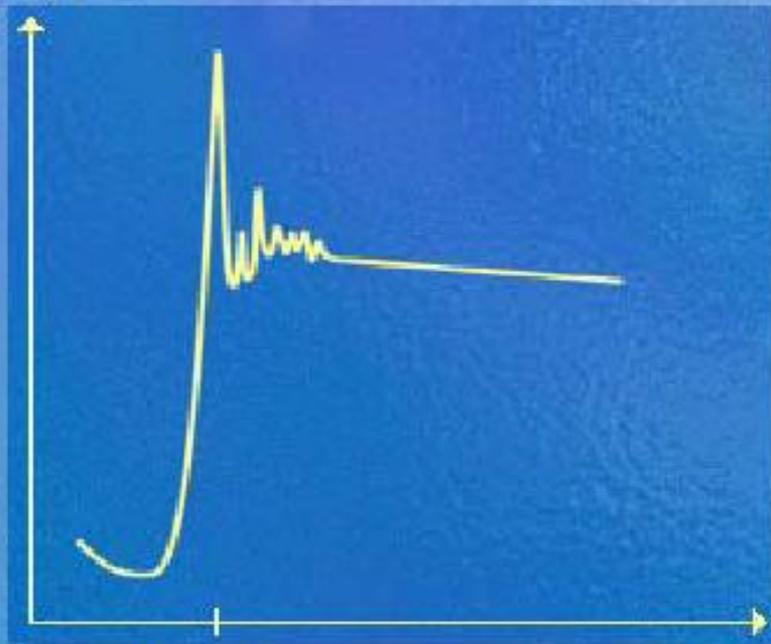
Many methods adapted for the study of matter using synchrotron light benefit from the particular features found in the energy region around an absorption edge.



Iodine and Gadolinium K-Absorption Edges

Рентгеновская спектроскопия вблизи края поглощения

Absorption



absorption
edge

Energy

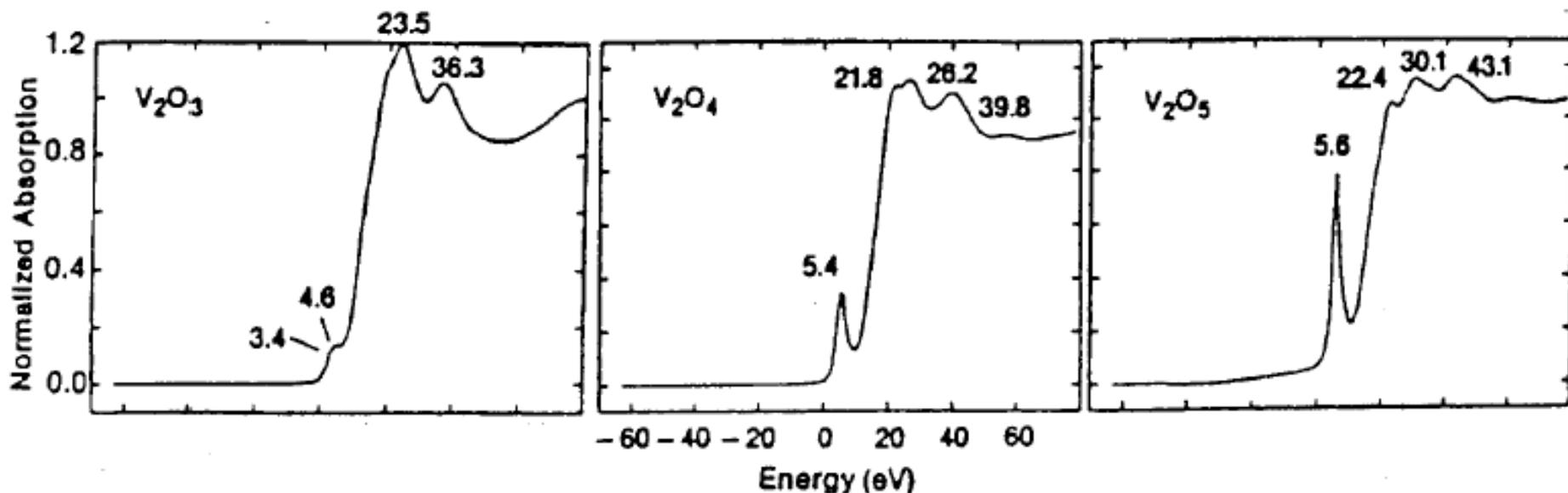
X-ray absorption spectroscopy

The x-ray absorption spectrum of a chemical element is obtained by exposing a sample of this element to a beam of x-rays, the energy of which is modified progressively. The absorption spectrum shows discontinuities which are called **absorption edges**. The study of these spectra is the basis of all types of x-ray absorption spectroscopy.

Amongst the methods developed for the use of synchrotron light, one should mention **EXAFS** and **XANES**, as well as **circular dichroism**.



Зависимость поглощения (XANES) от валентности и положения атома ванадия вблизи К-края поглощения



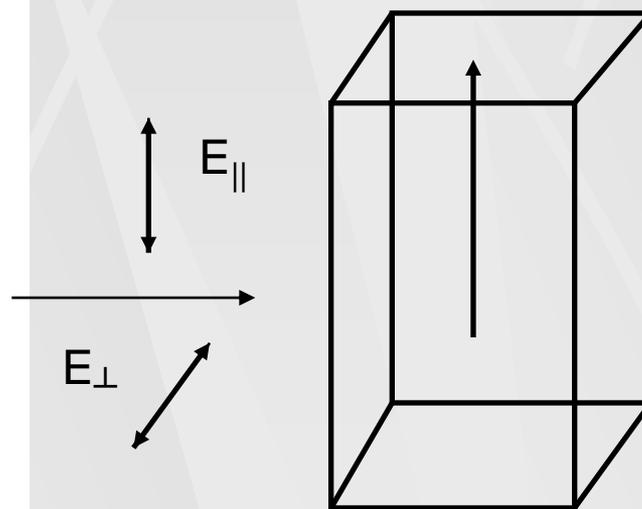
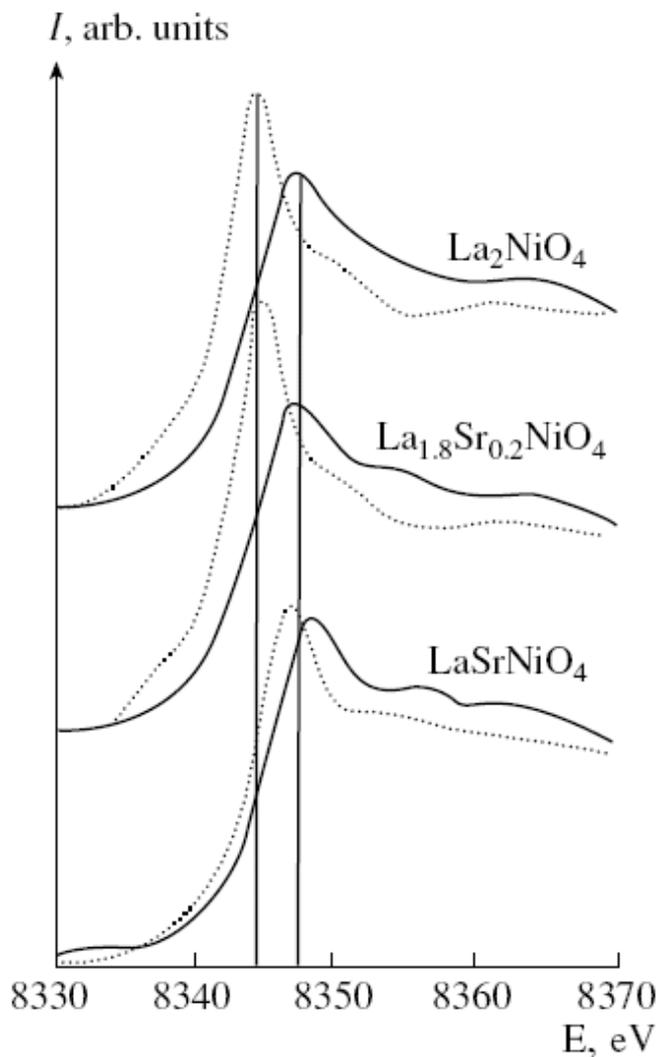
Здесь Energy - это энергия возбужденного фотоэлектрона

(картинка из Wong, J. et al. *Phys. Rev.* **1984**, B30, 5596)

А ещё поглощение зависит и от направления и от поляризации!

Поляризационная зависимость XANES: линейный дихроизм

Спектры поглощения вблизи К-края никеля для поляризаций параллельной оси (точки) и перпендикулярной (сплошная линия) поляризаций

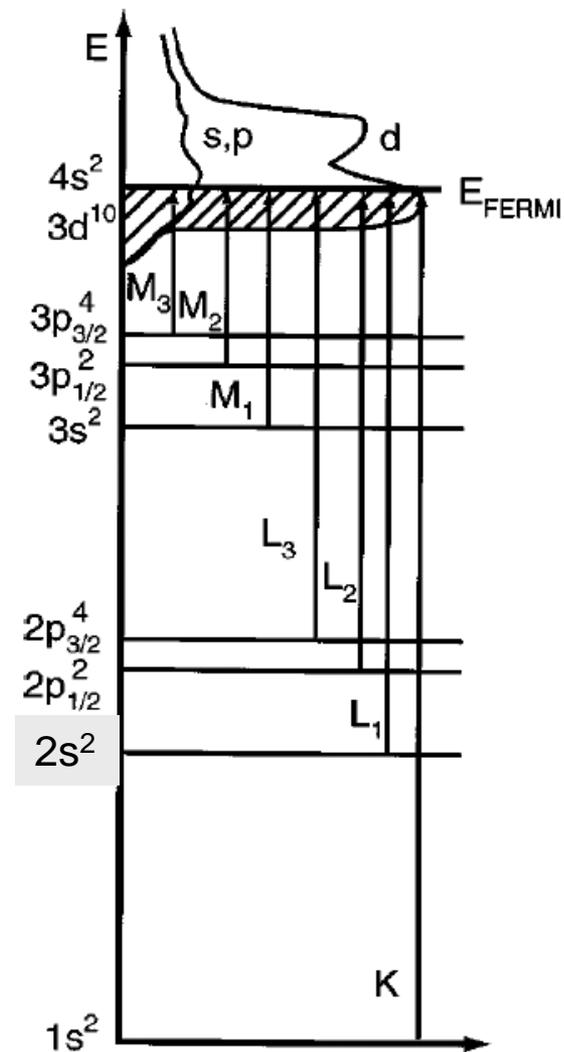


Откуда возникает зависимость от энергии и от поляризации

Зонная структура кристалла.

Сказывается также симметрия возбужденного состояния, т.е. вблизи края поглощения возбужденный электрон «чувствует» соседние атомы.

Надо ещё учитывать правила отбора при поглощении и рассеянии фотонов, наличие «дырки» с конечным временем жизни на начальном уровне и т.п.



The physics of resonant X-rays diffraction: a crucial role of electron scattering

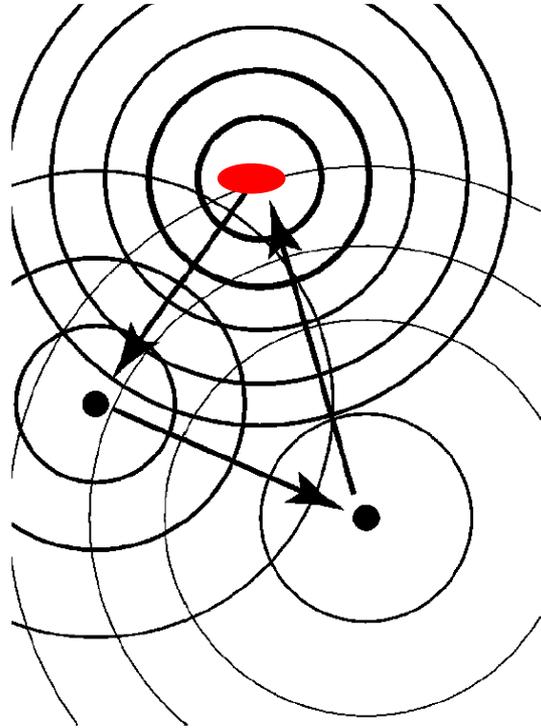
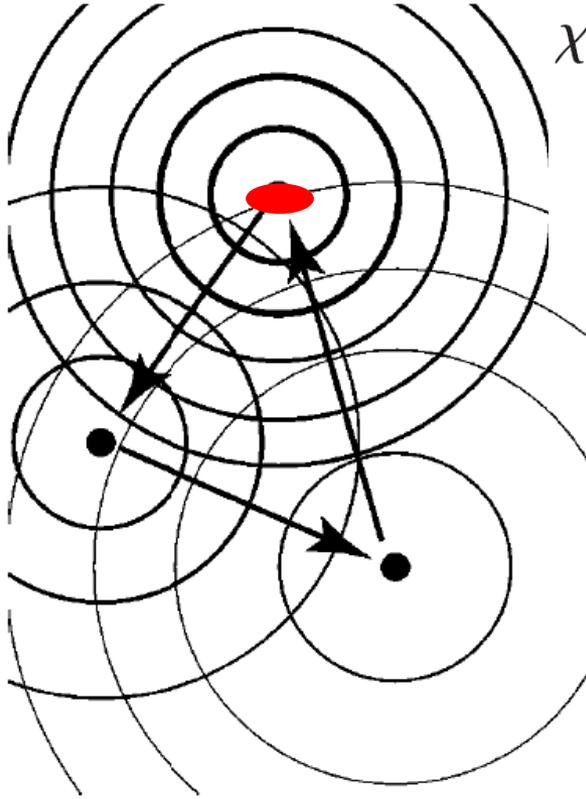


FIG. 5. Pictorial view of the multiple scattering of an outgoing wave off neighboring atoms. The topmost atom is the original source of the wave, which diffracts first off the atom at the lower left and finally off the atom at the lower right. Each successive outgoing spherical wave is weaker, which is reflected in the thickness of the spherical wave fronts. This type of path is called a triangular path.

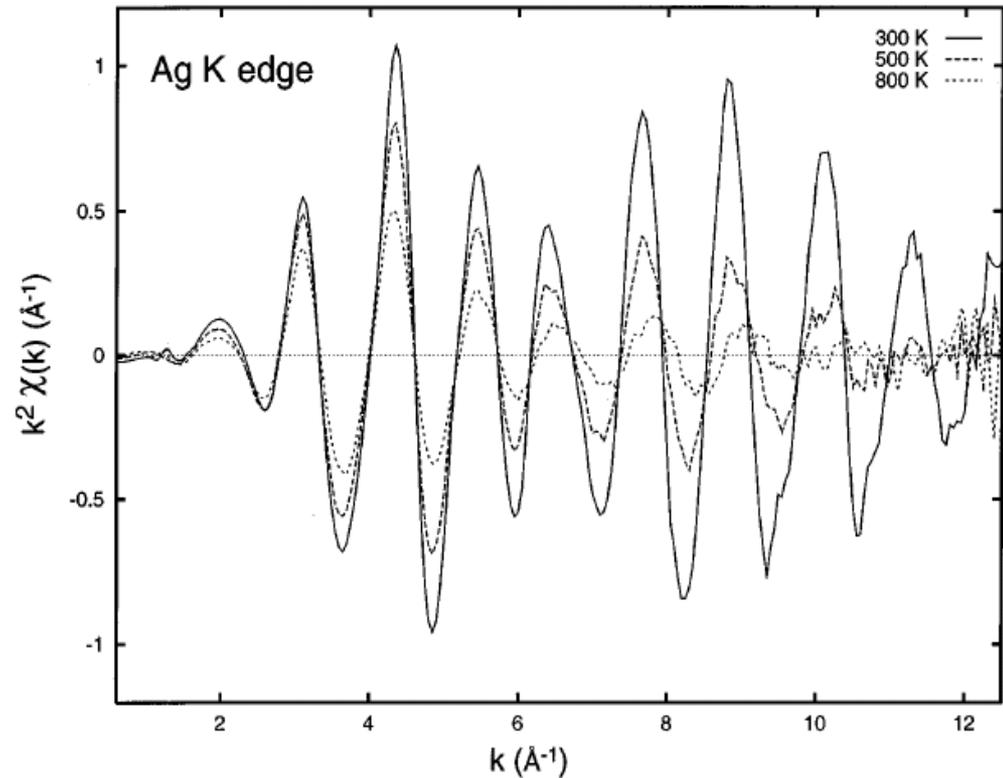
1. Typical energy interval < 50 eV above edges;
2. Multiple scattering of virtual electrons;
3. Sensitivity to environment;
4. Lifetime of virtual electrons;
5. Local and non-local effects
(dipole-dipole, dipole-quadrupole, etc.);

Область EXAFS (Extended X-ray Absorption Fine Structure)



$$\chi(k) = \sum_R S_0^2 N_R \frac{|f(k)|}{kR^2}$$

$$\times \sin(2kR + 2\delta_c + \Phi) e^{-2R/\lambda(k)} e^{-2\sigma^2 k^2}$$



Аномальные (резонансные) поправки к атомным факторам (амплитудам рассеяния)

$$f'_{jk} + if''_{jk} = \frac{m_e}{\hbar^3 \omega} \sum_{V,g} \frac{\langle \epsilon_V - E_g \rangle^3 \langle g | O_j^{'+} | V \rangle \langle V | O_k | g \rangle}{\hbar \omega - \langle \epsilon_V - E_g \rangle - i\Gamma/2}$$

$$O_i = \vec{e}_i \vec{r} \left(1 - \frac{1}{2} i \vec{k} \vec{r} \right) \quad O'_i = \vec{e}'_i \vec{r} \left(1 - \frac{1}{2} i \vec{k}' \vec{r} \right)$$

Эти вычисления очень сложны, и поэтому часто используют феноменологическое разложение тензора f по k, k' , $ka_{K,L,M} \ll 1$

$$f_{jk} = f_{jk}^{dd} + if_{jkm}^{dq,s} \langle \epsilon'_m - k_m \rangle + if_{jkm}^{dq,a} \langle \epsilon'_m + k_m \rangle + if_{jkmn}^{qq} k'_m k_n$$

Рассеяние вперед $k' = k$: поглощение, дихроизм оптическая активность;

$k' \neq k$: упругое и неупругое рассеяние, дифракция

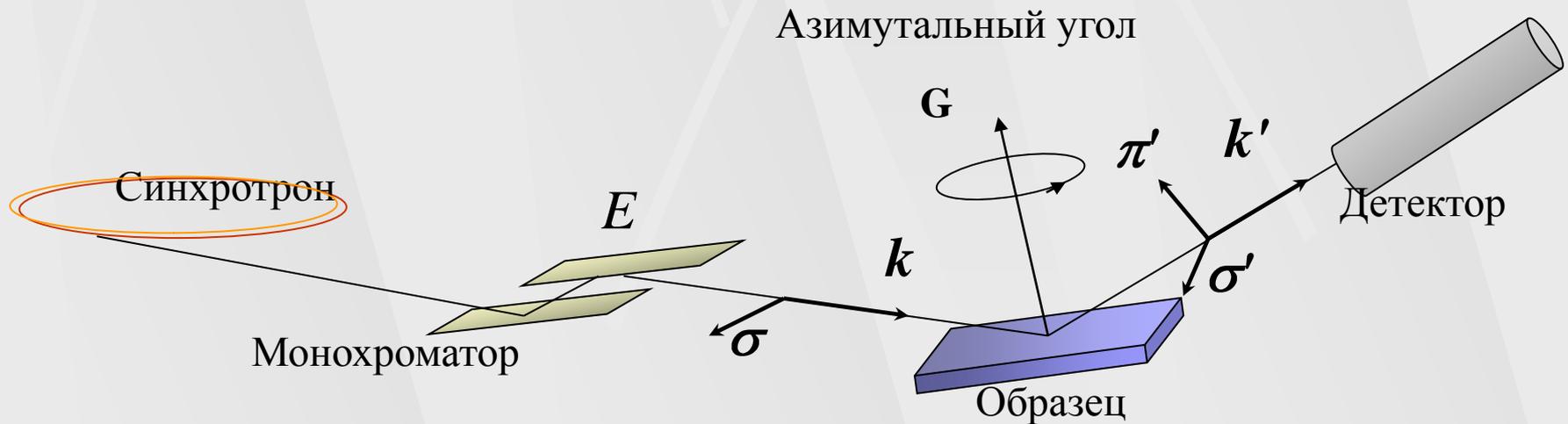
Resonant X-ray diffraction (RXD)

= diffraction @ XANES = XDNES = DAFS

- RXD is site-, element-, and shell-selective technique (e.g. XANES is not site-selective!)
- the resonant scattering amplitude depends on the orientations and electronic and magnetic states of both resonant and neighbouring atoms
- complicated polarization/azimuthal properties of “forbidden reflection” (rotation $\pi \leftrightarrow \sigma$, chirality)
- **drawbacks**: a modern synchrotron and smart modelling are needed

More details about “forbidden reflections” can be found in:
V. E. Dmitrienko, K. Ishida, A. Kirfel, E.N. Ovchinnikova,
Acta Crystallographica **A61** (2005) 481.

Резонансная дифракция: необходим синхротрон для работы вблизи края поглощения



Дифракционные методы

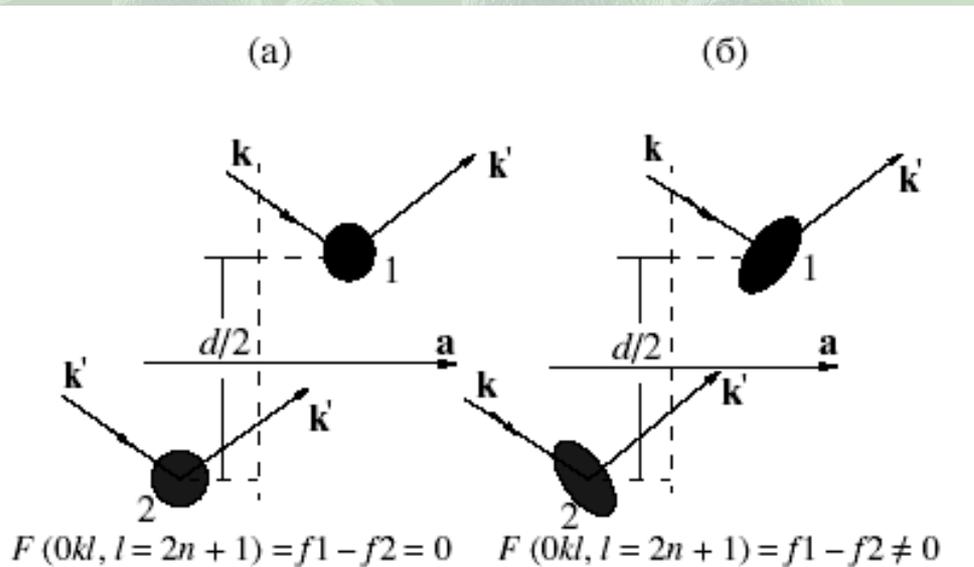
DAFS- Diffraction Anomalous Fine Structure
(дифракционная аномальная тонкая структура)

DANES – Diffraction Anomalous Near Edge Spectroscopy
(дифракционная аномальная спектроскопия вблизи края)

Resonant X-ray diffraction, Resonant X-ray Scattering (RXS)
(резонансная рентгеновская дифракция, рассеяние)

Magnetic X-ray Scattering (resonant and non-resonant)
(магнитное рассеяние рентгеновских лучей)

Чисто резонансные брэгговские рефлексы



Условия возникновения

1. Наличие погасаний вдали от края поглощения $F(H)=0$; следствие симметрии!!!!.
2. Отличие от нуля тензорного структурного фактора вблизи края поглощения $F(H) \neq 0$.

$$\hat{\chi}(\mathbf{r}) = \hat{R}_g \hat{\chi}(\mathbf{r}') \hat{R}_g^{-1}$$

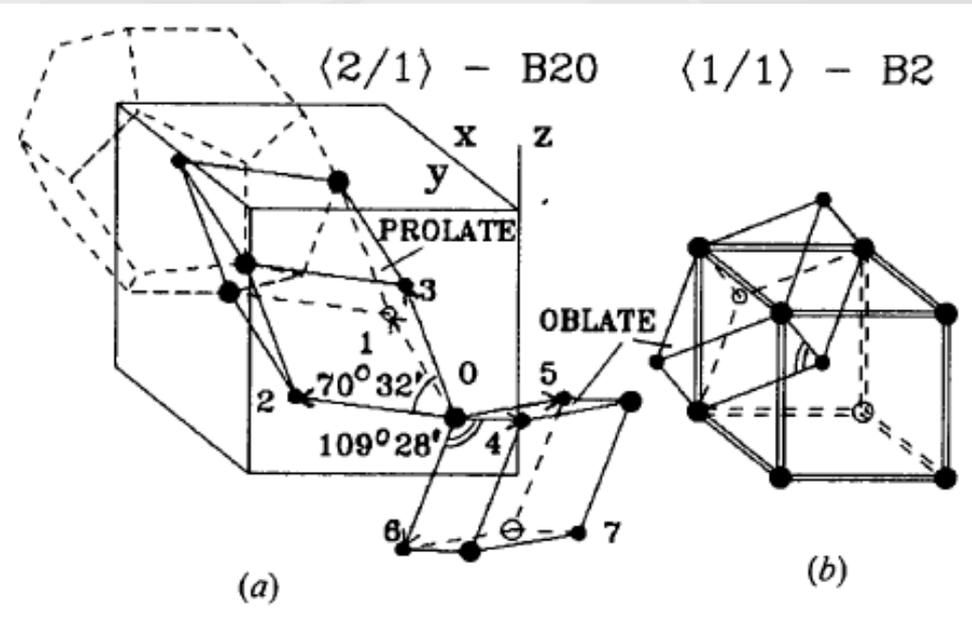
Возникновение «запрещенных» отражений вблизи краев поглощения связано с расщеплением электронных состояний в кристаллическом поле, с учетом спин-орбитального взаимодействия и других видов анизотропии.

Преимуществом использования чисто резонансных отражений является то, что они не содержат нерезонансных вкладов и имеют необычные поляризационные свойства

Симметричный подход

B20 – MnSi space group $P2_13$

Mn – 4 atoms, coordinates: x, x, x, \dots



$$\widehat{F}(00l) = \frac{4}{3}(f_{\parallel} - f_{\perp}) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\widehat{F}(0kl) = \frac{4}{3}(f_{\parallel} - f_{\perp}) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

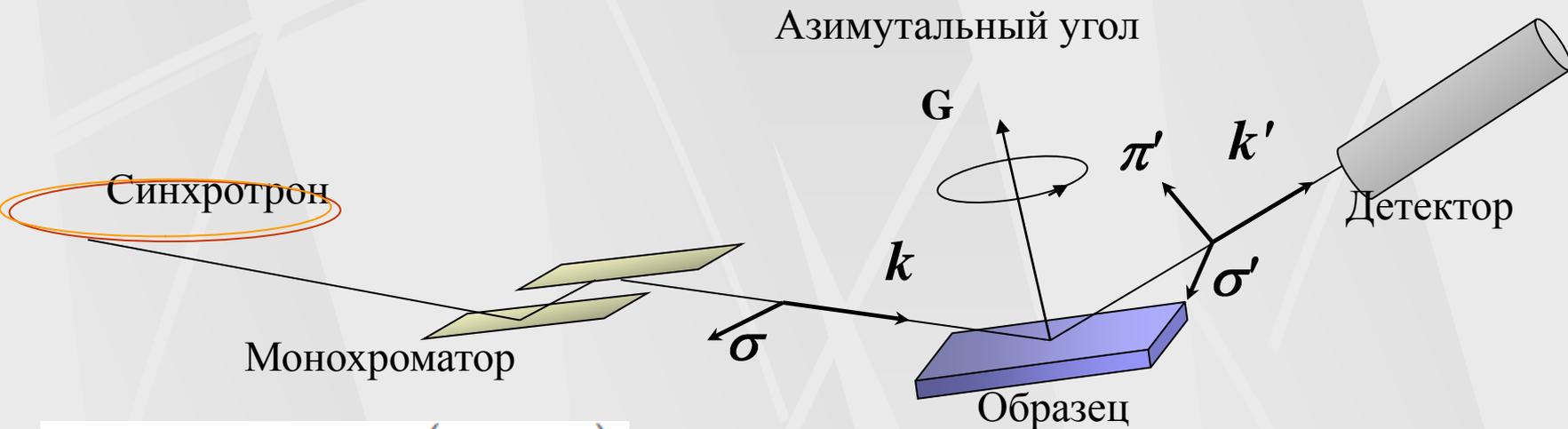
$$\hat{f}^1 = \begin{pmatrix} f_{xx} & f_{xy} & f_{xy} \\ f_{xy} & f_{xx} & f_{xy} \\ f_{xy} & f_{xy} & f_{xx} \end{pmatrix}$$

$$\hat{f}^2 = \begin{pmatrix} f_{xx} & -f_{xy} & -f_{xy} \\ -f_{xy} & f_{xx} & f_{xy} \\ -f_{xy} & f_{xy} & f_{xx} \end{pmatrix}$$

$$\hat{f}^3 = \begin{pmatrix} f_{xx} & -f_{xy} & f_{xy} \\ -f_{xy} & f_{xx} & -f_{xy} \\ f_{xy} & -f_{xy} & f_{xx} \end{pmatrix}$$

$$\hat{f}^4 = \begin{pmatrix} f_{xx} & f_{xy} & -f_{xy} \\ f_{xy} & f_{xx} & -f_{xy} \\ -f_{xy} & -f_{xy} & f_{xx} \end{pmatrix}$$

Симметричный подход: поляризационные свойства



$$\hat{F}(00l) = \frac{4}{3}(f_{\parallel} - f_{\perp}) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\hat{F}(0kl) = \frac{4}{3}(f_{\parallel} - f_{\perp}) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$I_{\sigma\sigma} = |\sigma \hat{F}^H \sigma|^2$$

$$I_{\pi\pi} = |\pi_H \hat{F}^H \pi_0|^2$$

$$I_{\sigma\pi} = I_{\pi\sigma} = |\pi_H \hat{F}^H \sigma|^2 = |\sigma \hat{F}^H \pi_0|^2$$

B20 – MnSi space group $P2_13$

Mn – coordinates: x,x,x

Симметричный подход: координаты атомов

$$|\sigma \hat{F} \pi|^2 = \frac{8}{9} |f_{\parallel} - f_{\perp}|^2 \cos^2 \theta (1 - \cos 4\pi l x \cos 2\psi)$$

ψ – азимутальный угол

Templeton, D. H. & Templeton, L. K. (1986). *Acta Cryst.* A42, 478–481.

NaBrO₃ – space group P2₁3

Br – coordinates: x, x, x

$$\hat{F}(00l) = \frac{4}{3} (f_{\parallel} - f_{\perp}) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

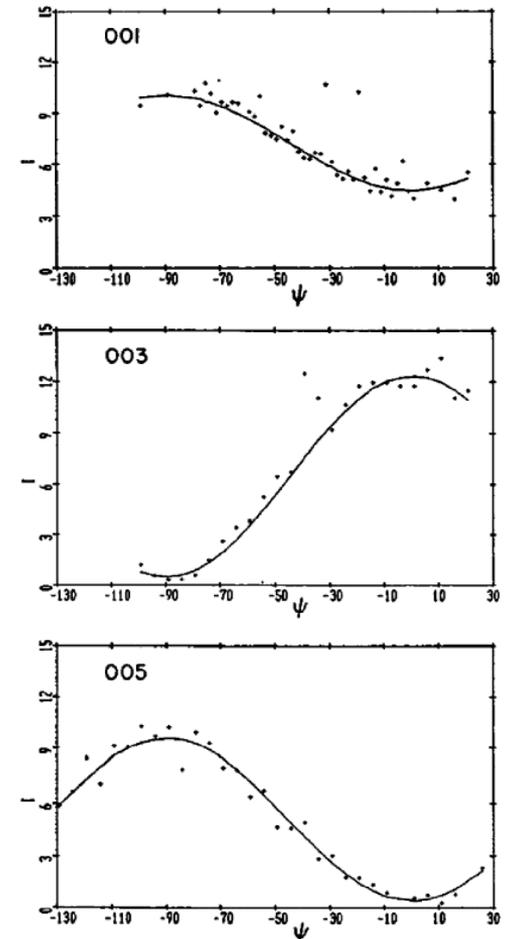
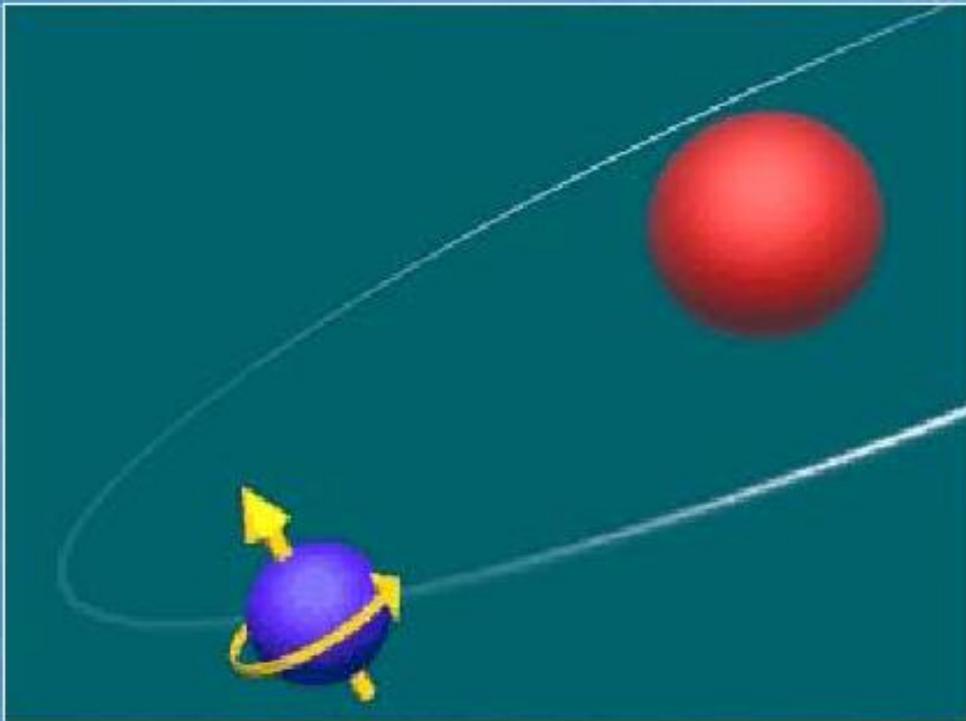


Figure 1
Observed (points) and calculated (lines) squares of structure factors for 001, 003 and 005 plotted as a function of azimuthal angle, at a photon energy 8 eV below the Br K white-line peak. A few high points, and another too far off scale to plot, indicate coincidence with Renninger reflections; this is Fig. 1 by Templeton & Templeton (1986).

Магнитная дифракция

Methods

X-ray diffraction



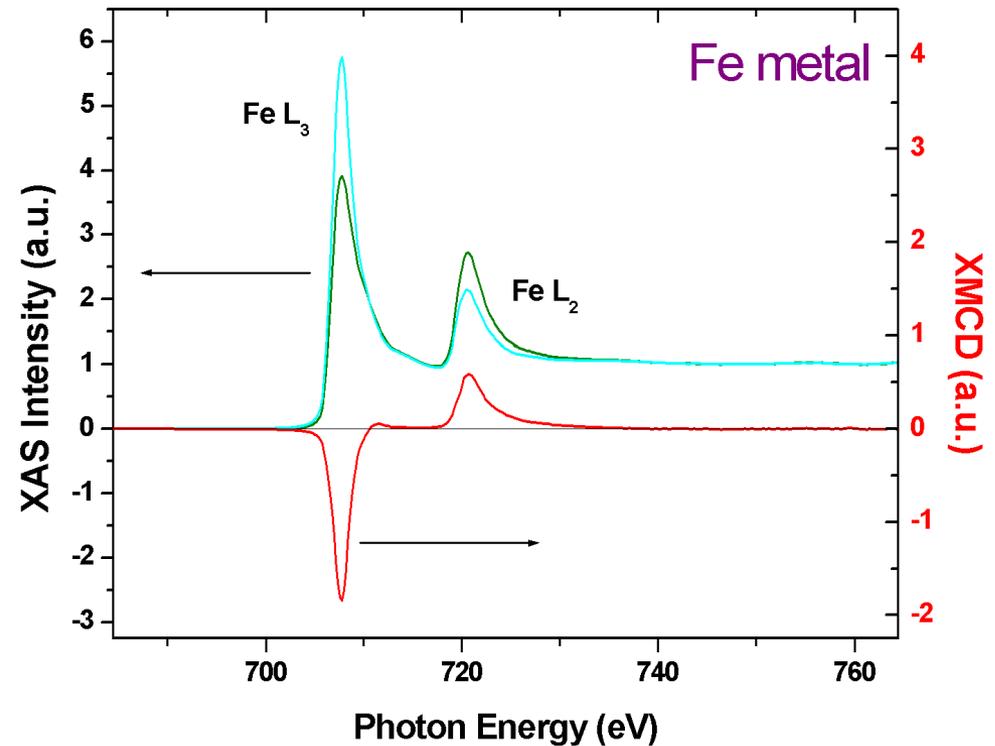
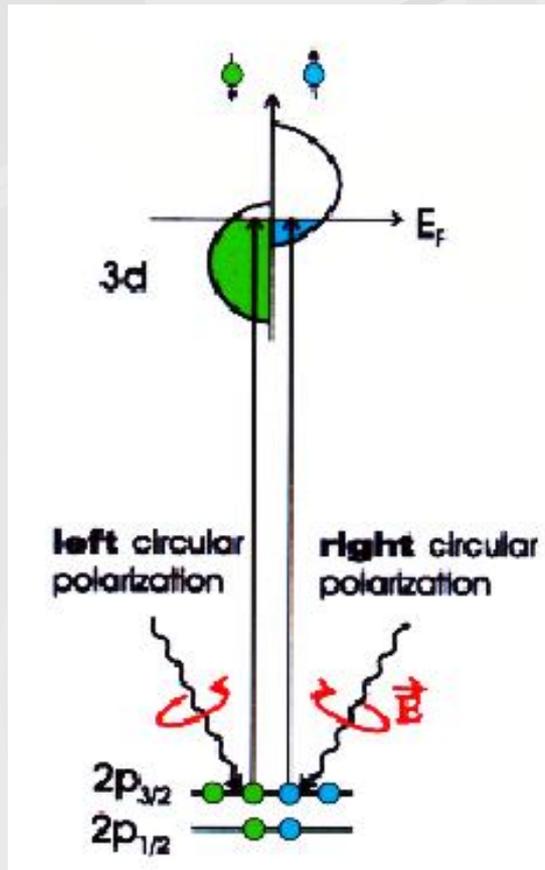
Specific diffraction methods

Magnetic diffraction

Magnetic diffraction arises due to the interaction of x-rays (electromagnetic waves) with the magnetic properties of electrons (orbital magnetism or spin magnetism). These studies require that the light be linear or circular polarized. Resonant magnetic diffraction experiments require that the x-ray energy be adjusted to an energy near the absorption edges of the sample (as in anomalous scattering). This increases the magnetic signal by a factor which can go up to 1,000,000 depending on the atoms being considered. Synchrotron light is perfectly adapted to these studies where it is necessary to be able to adjust the energy and polarization of the photons.

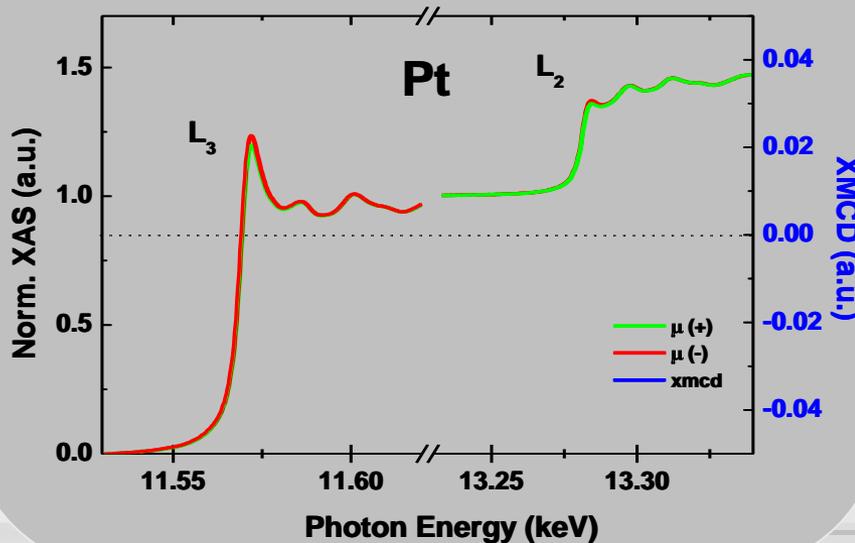
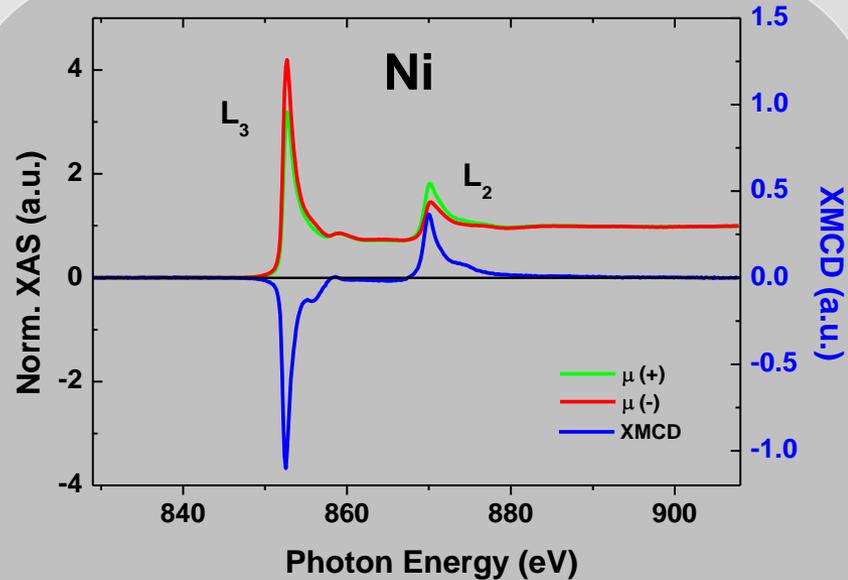
TWO STEP MODEL OF XMCD

Exchange splitting of the valence band is driving the second step



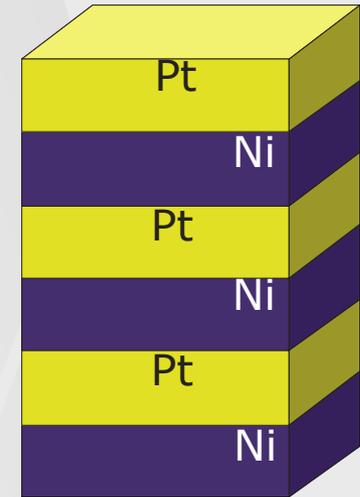
Магнитное рассеяние – конкурент нейтронам

Element and Orbital Selectivity of XMCD



Ni₂/Pt₂ multilayer

T ~ 10K
H = ± 5 T



RESULTS

- Ni magnetic moments:

$$\mu_S^{3d} = 0.35 \mu_B/\text{atom}$$

$$\mu_L^{3d} = 0.038 \mu_B/\text{atom}$$

- Pt induced magnetic moments:

$$\mu_S^{5d} = 0.14 \mu_B/\text{atom}$$

$$\mu_L^{5d} = 0.03 \mu_B/\text{atom}$$

Классическая картина рассеяния

F. de Bergevin, M. Brunel, Acta Cryst. A 37 (1981) 314–331
 F. de Bergevin, M. Brunel, Acta Cryst. A 37 (1981) 324–331

Запрещенный рефлекс 111 в Fe_2O_3

- Возможно разделение спинового и орбитального вкладов

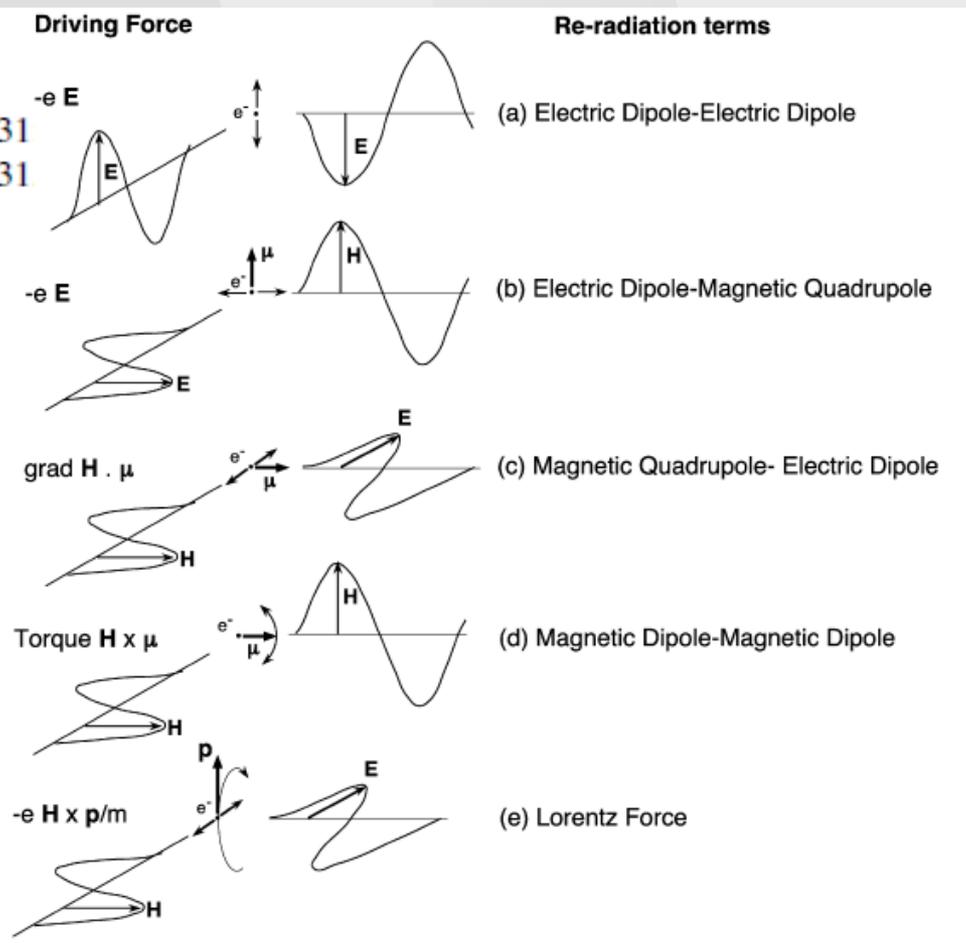


Fig. 1. Classical representation of the dominant scattering mechanisms of the photon–electron interaction [11].

Квантовая картина

- Гамильтониан взаимодействия

$$\begin{aligned} \mathcal{H}' &= \mathcal{H}'_1 + \mathcal{H}'_2 + \mathcal{H}'_3 + \mathcal{H}'_4 \\ &= \frac{e^2}{2mc^2} \sum_j \mathbf{A}^2(\mathbf{r}_j) - \frac{e}{mc} \sum_j \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{P}_j - \frac{e\hbar}{mc} \sum_j \mathbf{s}_j \cdot [\nabla \times \mathbf{A}(\mathbf{r}_j)] \\ &\quad - \frac{e\hbar}{2(mc)^2} \frac{e}{c^2} \sum_j \mathbf{s}_j \cdot [\dot{\mathbf{A}}(\mathbf{r}_j) \times \mathbf{A}(\mathbf{r}_j)] \end{aligned}$$

- Теория возмущений дает резонансный и нерезонансный вклады в атомный фактор рассеяния

$$\begin{aligned} f_n(\mathbf{k}, \mathbf{k}', \hat{\epsilon}, \hat{\epsilon}', \hbar\omega) &= \langle a | \sum_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} | a \rangle \hat{\epsilon}' \cdot \hat{\epsilon} - i \frac{\hbar\omega}{mc^2} \langle a | \sum_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} \left[\frac{i\mathbf{Q} \times \mathbf{P}_j}{\hbar k^2} \cdot \mathbf{A}' + \mathbf{s}_j \cdot \mathbf{B}' \right] | a \rangle \\ &\quad + \frac{1}{m} \sum_c \frac{E_a - E_c}{\hbar\omega_k} \left(- \frac{\langle a | O^+(\mathbf{k}') | c \rangle \langle c | O(\mathbf{k}) | a \rangle}{E_a - E_c + \hbar\omega_k - i\Gamma_c/2} + \frac{\langle a | O(\mathbf{k}) | c \rangle \langle c | O^+(\mathbf{k}') | a \rangle}{E_a - E_c - \hbar\omega_k} \right) \end{aligned}$$

Жижимов О Л, Хриплович И Б // ЖЭТФ 1984 Т 87 С 547.
Blume M // J App Phys 1985 V 57 P 3615

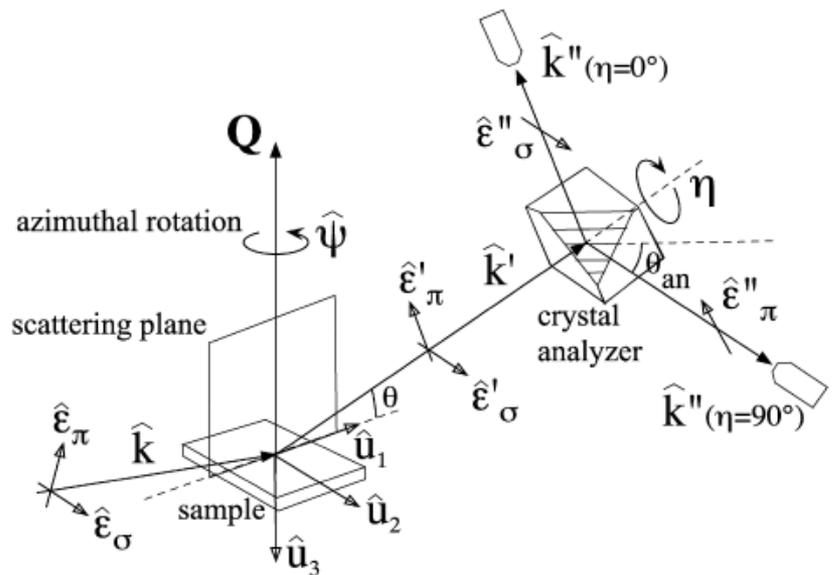
M. Blume, Resonant anomalous X-ray scattering, in: G. Materlik, J. Sparks, K. Fisher (Eds.), Elsevier Science B.V., Amsterdam, 1994, pp. 495–512.

Разделение спинового и орбитального вкладов

- Вдали от края поглощения

$$S(\mathbf{Q}) = \langle a | \sum_j s_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} | a \rangle$$

$$L(\mathbf{Q}) = \langle a | \sum_j l_j e^{i\mathbf{Q} \cdot \mathbf{r}_j} | a \rangle$$



$$f^{\text{magn.}} = -i \frac{\hbar \omega}{mc^2} \left(\frac{1}{2} L(\mathbf{Q}) \cdot \mathbf{A}'' + S(\mathbf{Q}) \cdot \mathbf{B}' \right)$$

$$= -i \frac{\hbar \omega}{mc^2} \begin{pmatrix} M_{\sigma\sigma} & M_{\pi\sigma} \\ M_{\sigma\pi} & M_{\pi\pi} \end{pmatrix}$$

$$M_{\sigma\sigma} = S_2 \sin 2\theta$$

$$M_{\pi\sigma} = -2 \sin^2 \theta [(\cos \theta)(L_1 + S_1) - S_3 \sin \theta]$$

$$M_{\sigma\pi} = 2 \sin^2 \theta [\cos \theta (L_1 + S_1) + S_3 \sin \theta]$$

$$M_{\pi\pi} = \sin 2\theta [2L_2 \sin^2 \theta + S_2]$$

Резонансные вклады: конкуренция магнитной и зарядовой анизотропии

Возможны комбинированные рефлексы

$$\chi_+^{\alpha\beta} = (n^\alpha n^\beta - \frac{1}{3}\delta^{\alpha\beta})[a_1 + b_1(\mathbf{n} \cdot \mathbf{m})^2]$$

$$+ c_1(m^\alpha m^\beta - \frac{1}{3}m^2\delta^{\alpha\beta})$$

$$+ d_1[n^\alpha m^\beta + n^\beta m^\alpha - \frac{2}{3}(\mathbf{n} \cdot \mathbf{m})\delta^{\alpha\beta}](\mathbf{n} \cdot \mathbf{m})$$

$$\chi_-^{\alpha\beta} = i\varepsilon^{\alpha\beta\gamma}[a_2 m^\gamma + b_2 n^\gamma (\mathbf{n} \cdot \mathbf{m})].$$

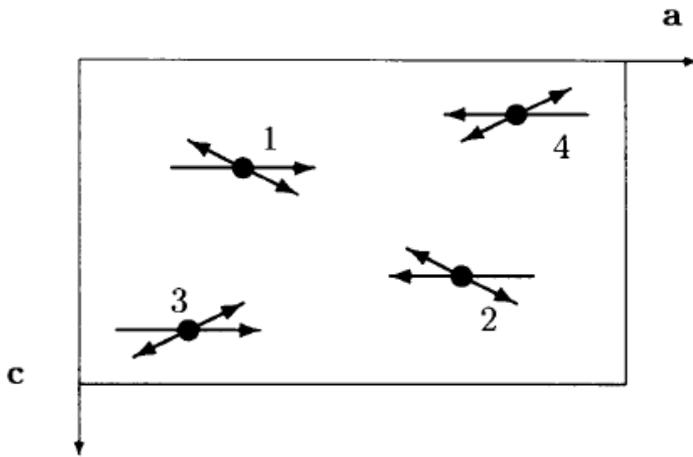


Fig. 2. The directions of the local crystal-field axes \mathbf{n}_i (double-ended arrows) and of the magnetic moments \mathbf{m}_i (arrows) corresponding to the G_x structure on the atoms in the $4(c)$ position of the $Pnma$ space group. All atoms lie on two mirror planes perpendicular to the b axis. The y coordinates for atoms 1 and 4 are equal to $b/4$, for 2 and 3, they are equal to $3b/4$.

Симметричный и
антисимметричный вклад

V₂O₃ – различные вклады

564

L. Paolasini, F. de Bergevin / C. R. Physique 9 (2008) 550–569

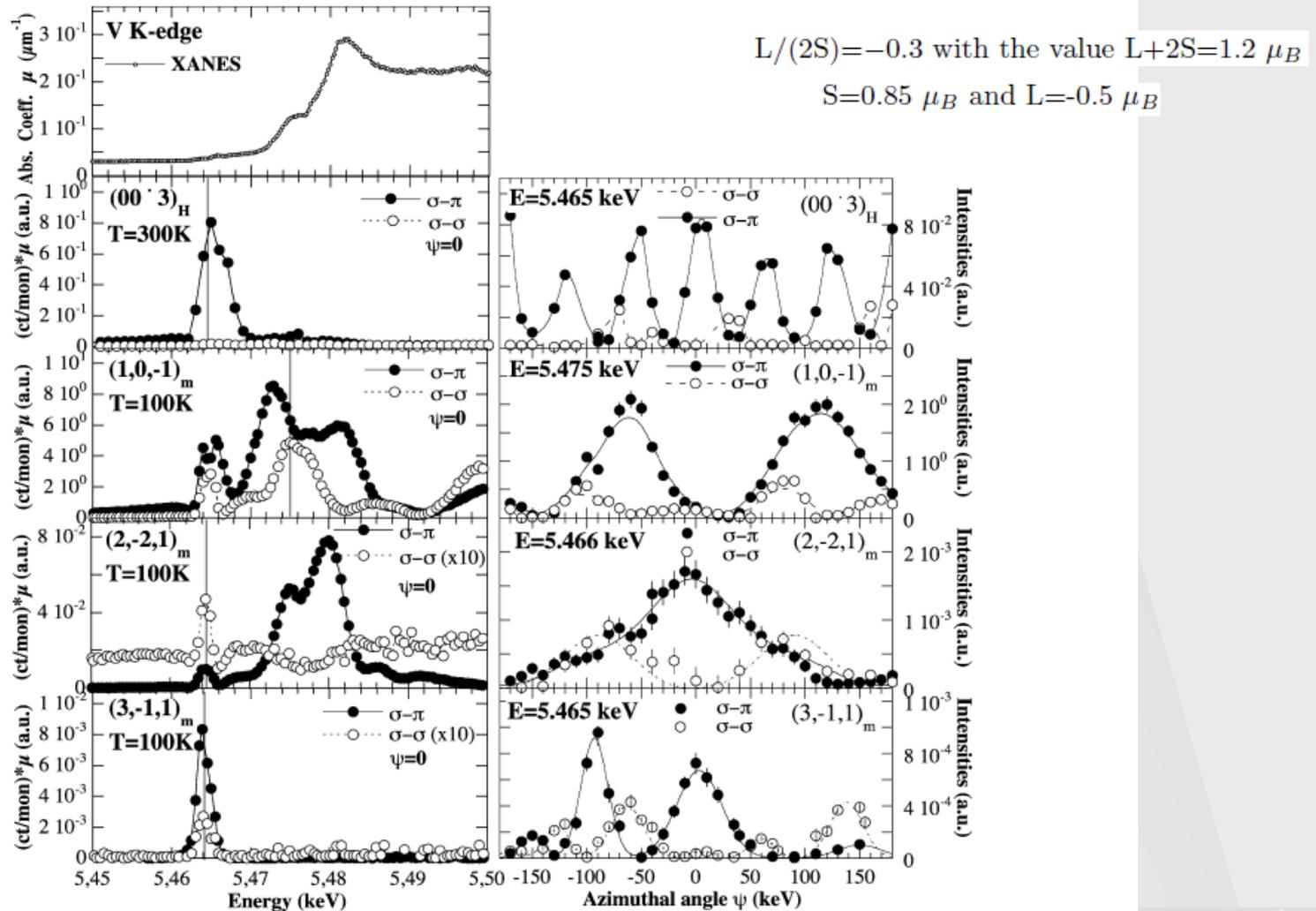
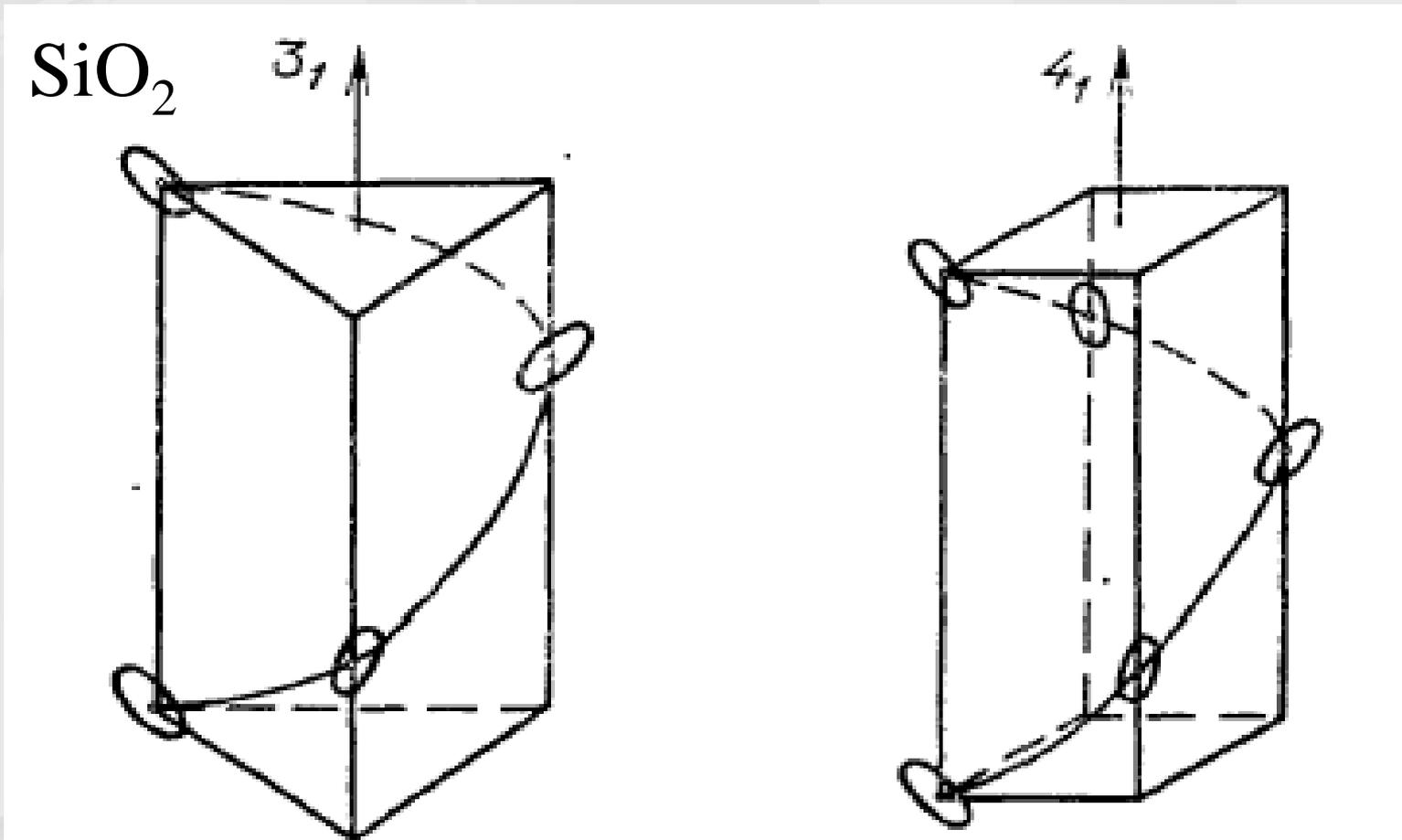


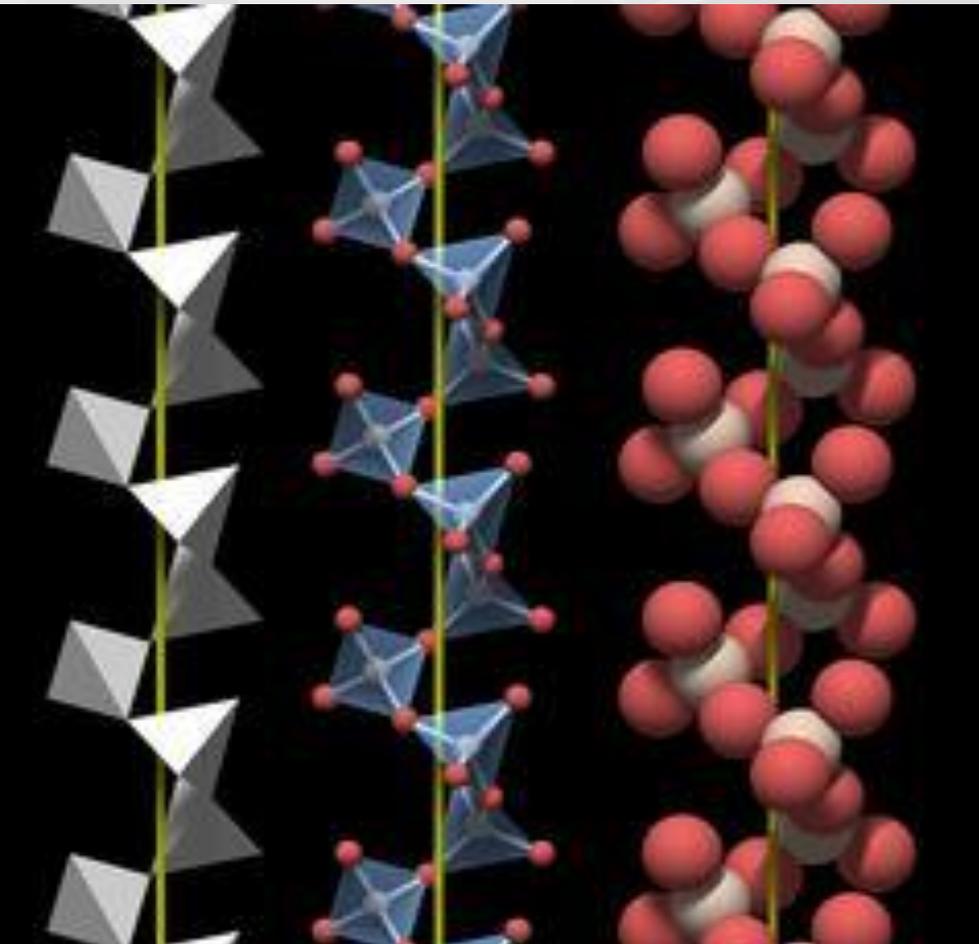
Fig. 4. Energy scans across the V K-edge (left) and the corresponding azimuthal dependence (right) of different classes of forbidden lattice reflections found at room temperature and in the low-temperature antiferromagnetic phase ($T = 100$ K) of 2.8% Cr-doped V₂O₃. Black (white) dots refer to the σ - π' (σ - σ') polarization channel [17,34].

Резонансная дифракция и «запрещённые» рефлексы (винтовые оси, часть 2)



Необычные поляризационные свойства!!!

Эффекты хиральности в кварце SiO_2



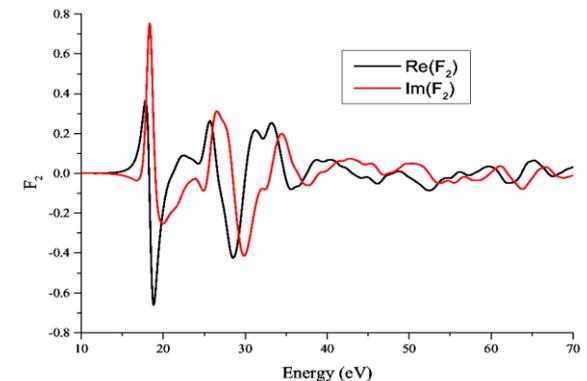
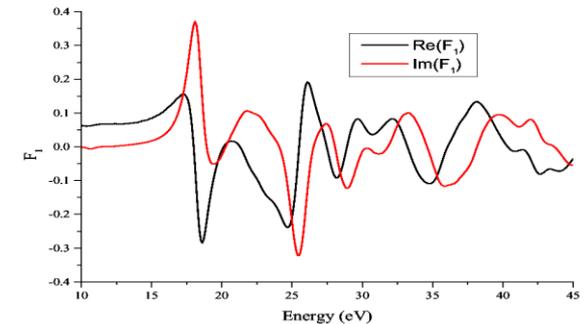
Threefold helices of SiO_4 “tetrahedra” in α -quartz
www.quartzpage.de/gen_struct.html

From the Fedorov space symmetry:

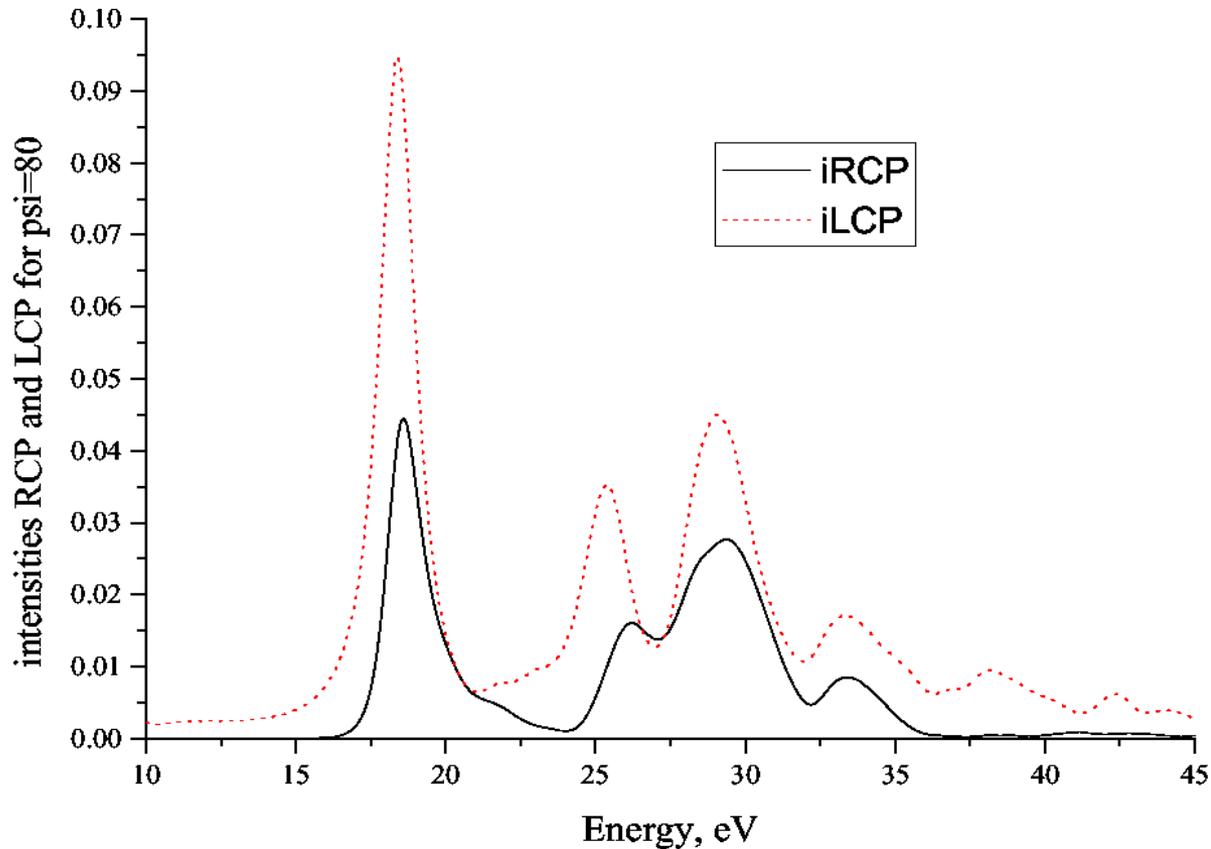
The tensor structure factor of 001 reflection in α -quartz depends on two parameters:

$$F_{jkl}(001) = \begin{pmatrix} F_1 & iF_1 & F_2 \\ iF_1 & -F_1 & -iF_2 \\ F_2 & -iF_2 & 0 \end{pmatrix}$$

ab initio simulations:
energy dependence of
coefficients F_1 and F_2

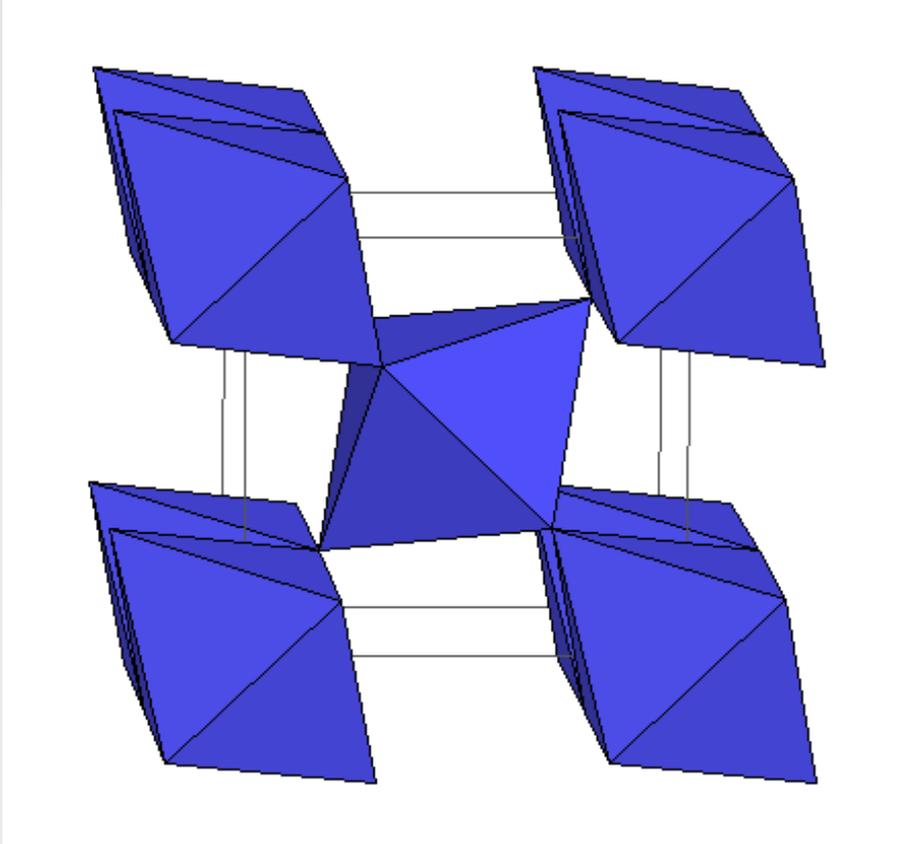


Сильная хиральность рефлекса 001 в кварце

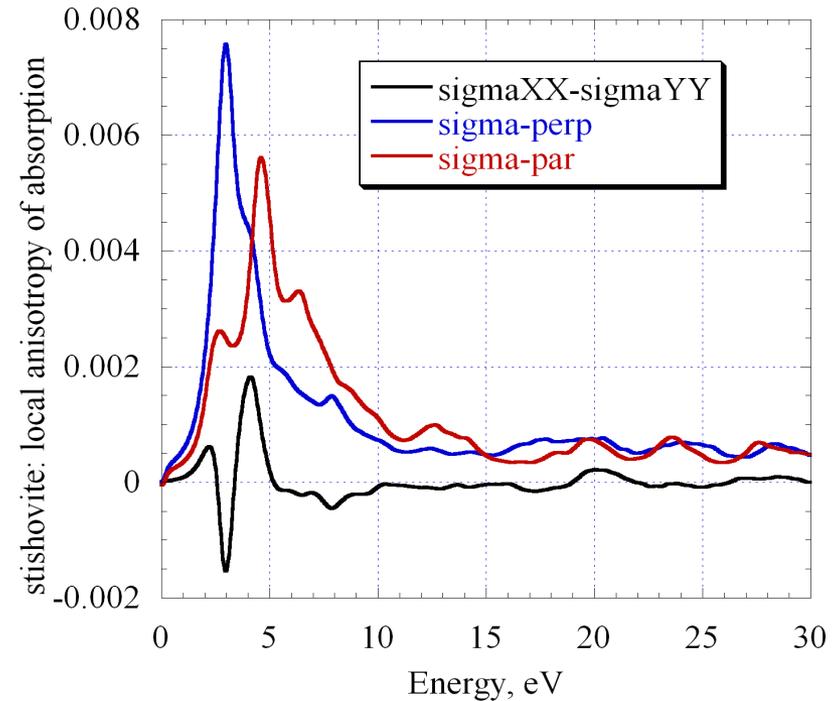


intensity of the 001 reflection is very different for Right and Left Circular Polarizations

Запрещенный рефлекс 100 в стишовите SiO_2 (плоскость скользящего отражения)

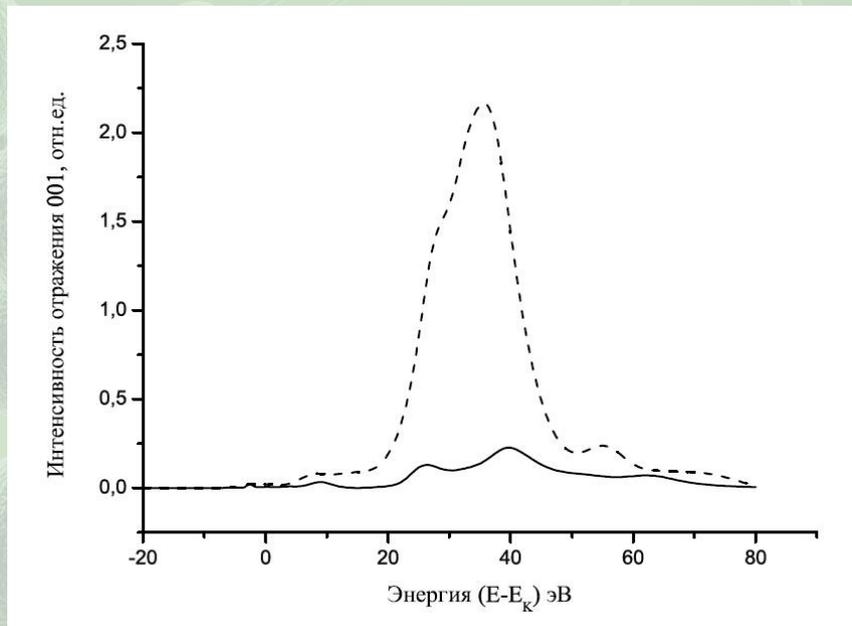
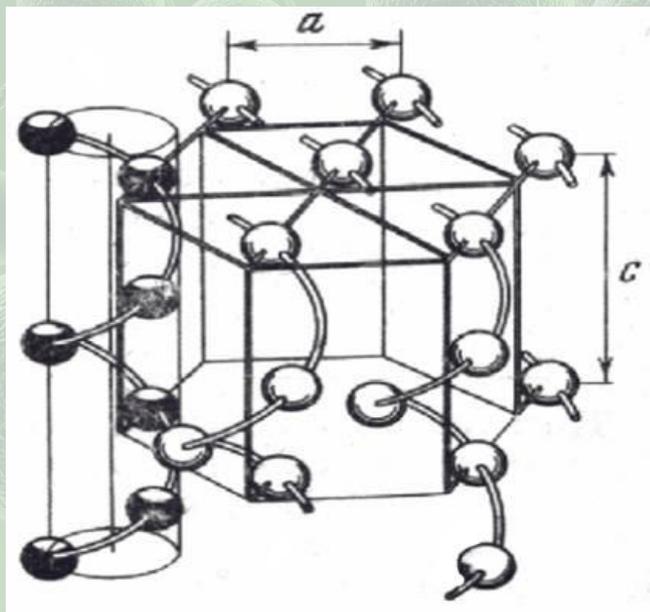


SiO_6 “octahedra” in stishovite
(rutile structure)



In stishovite, our *ab initio* calculations predict very strong local anisotropy and dichroism; the 100 reflection is **not chiral**.

Чисто-резонансные рефлекссы $0,0,3n+1$ в кристалле Те



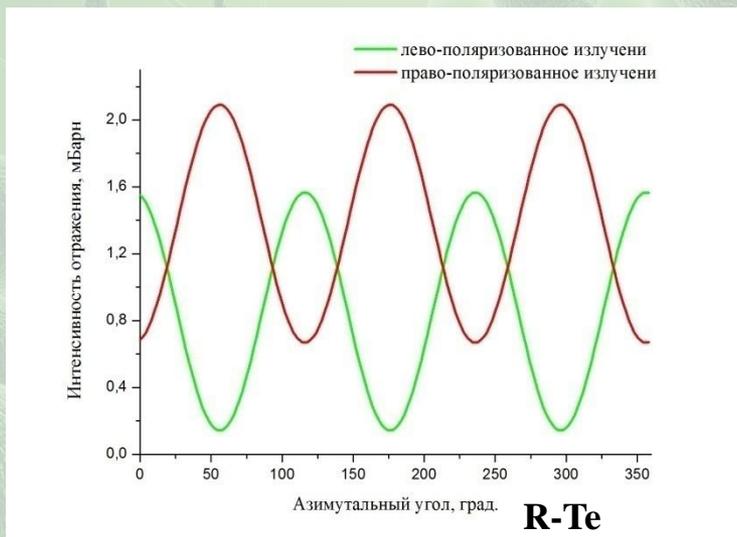
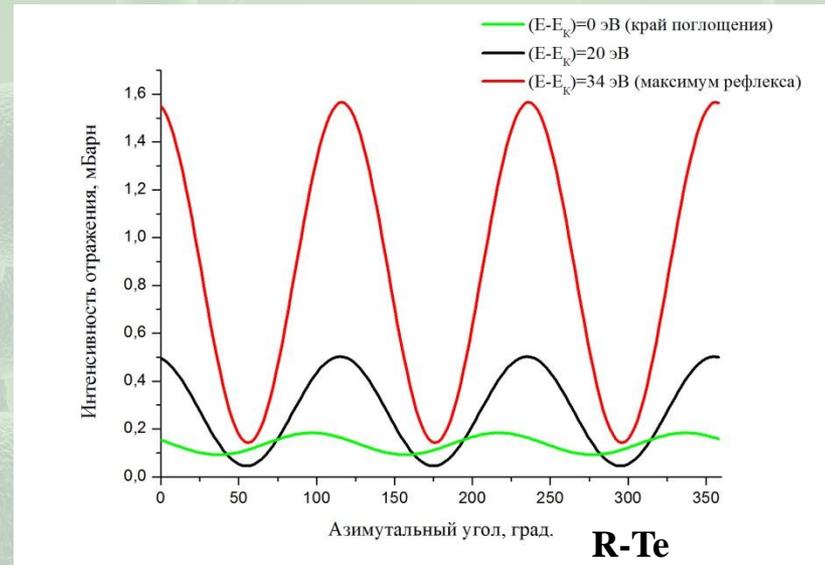
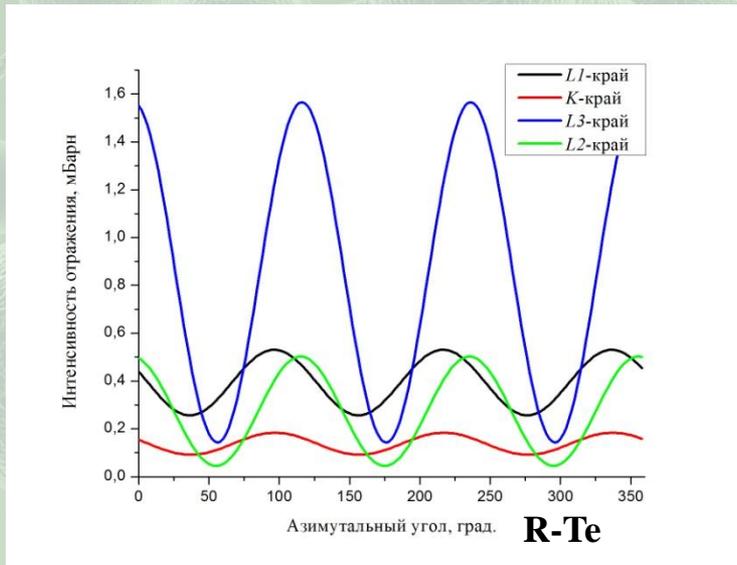
Теллур кристаллизуется в гексагональной решетке, пространственные группы **$P3_121$** и **$P3_221$** в случае правой и левой модификаций соответственно.

Параметры ячейки **$a = 0,44566$ нм**, **$c = 0,59268$ нм**.

Энергетический спектр чисто резонансного рефлекса 001 вблизи L3-края поглощения теллура для правой и левой модификациях кристалла.

Сплошная линия -- спектр рефлекса 001 для правого изомера;
пунктирная линия -- спектр рефлекса 001 для левого изомера.

Моделирование азимутальных зависимостей интенсивности отражений типа 001 на краях поглощения Te



Резонансная дифракция в кристалле пирита FeS_2

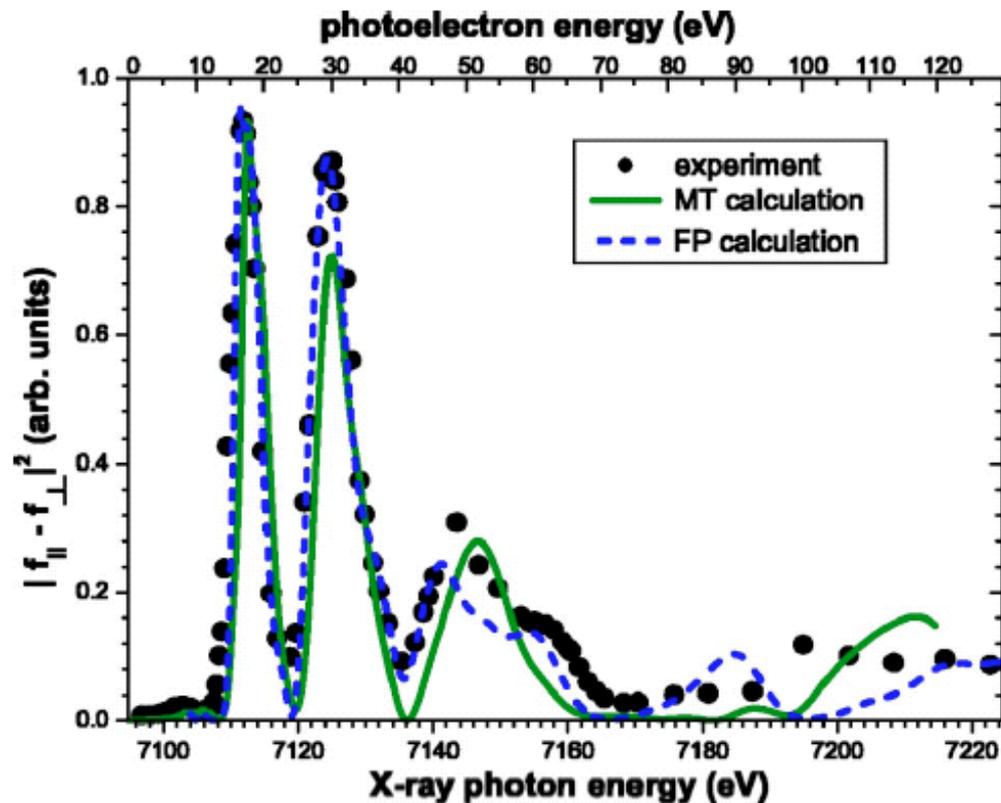
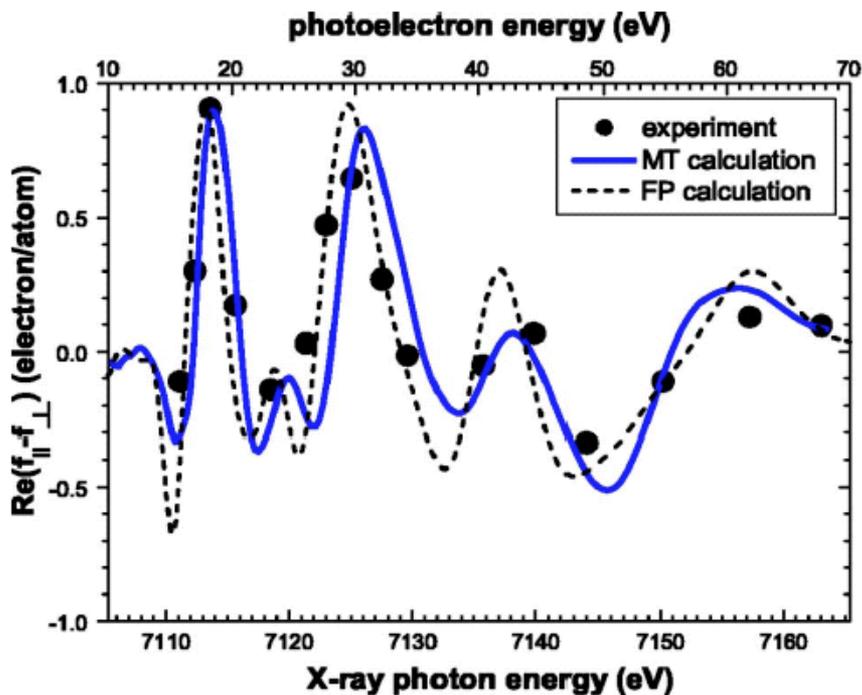


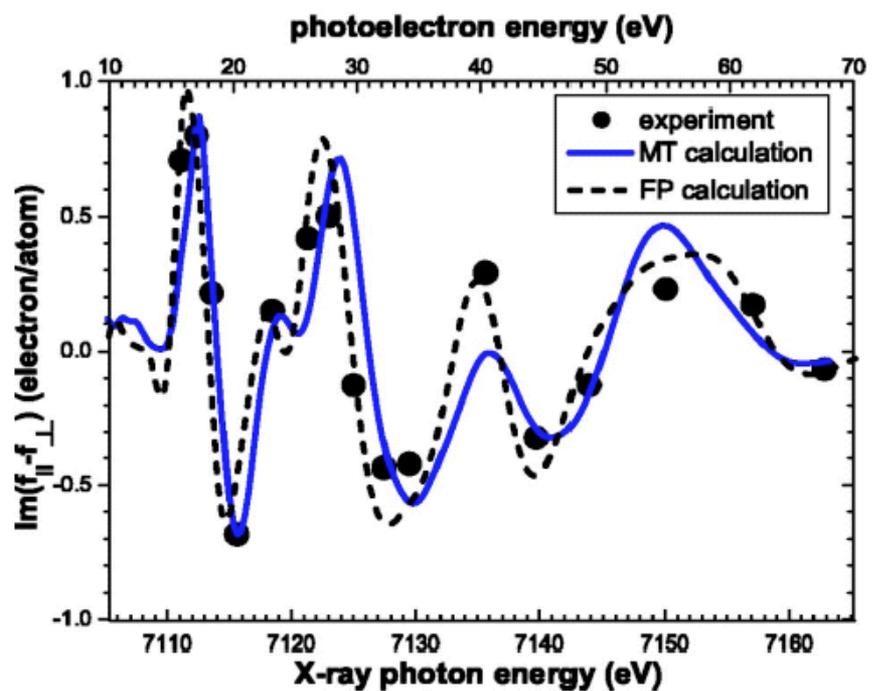
FIG. 10. (Color online) Experimental and theoretical ATS spectra near the Fe K edge. The experimental spectrum shows the intensity of the forbidden reflection corrected for absorption. The theoretical spectra are proportional to $|f_{||} - f_{\perp}|^2$.

Экспериментальное решение фазовой проблемы + расчеты ab initio для FeS₂

PHYSICAL REVIEW B 69, 245103 (2004)



(a)



(b)

FIG. 11. (Color online) Experimental $\text{Re}(f_{\parallel} - f_{\perp})$ (left) and $\text{Im}(f_{\parallel} - f_{\perp})$ (right) values (on absolute scale) as functions of the photon energy in comparison to FP and MT calculations.

Резонансная дифракция **мягкого** рентгеновского излучения в **сверхпроводнике** вблизи L-края меди

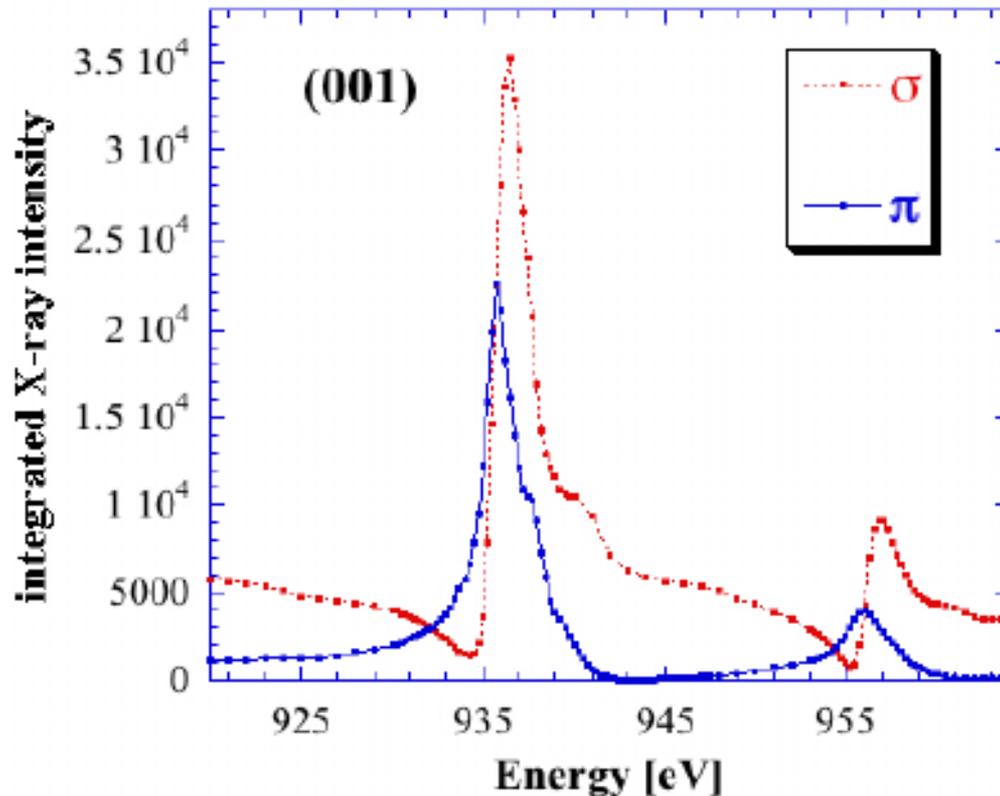


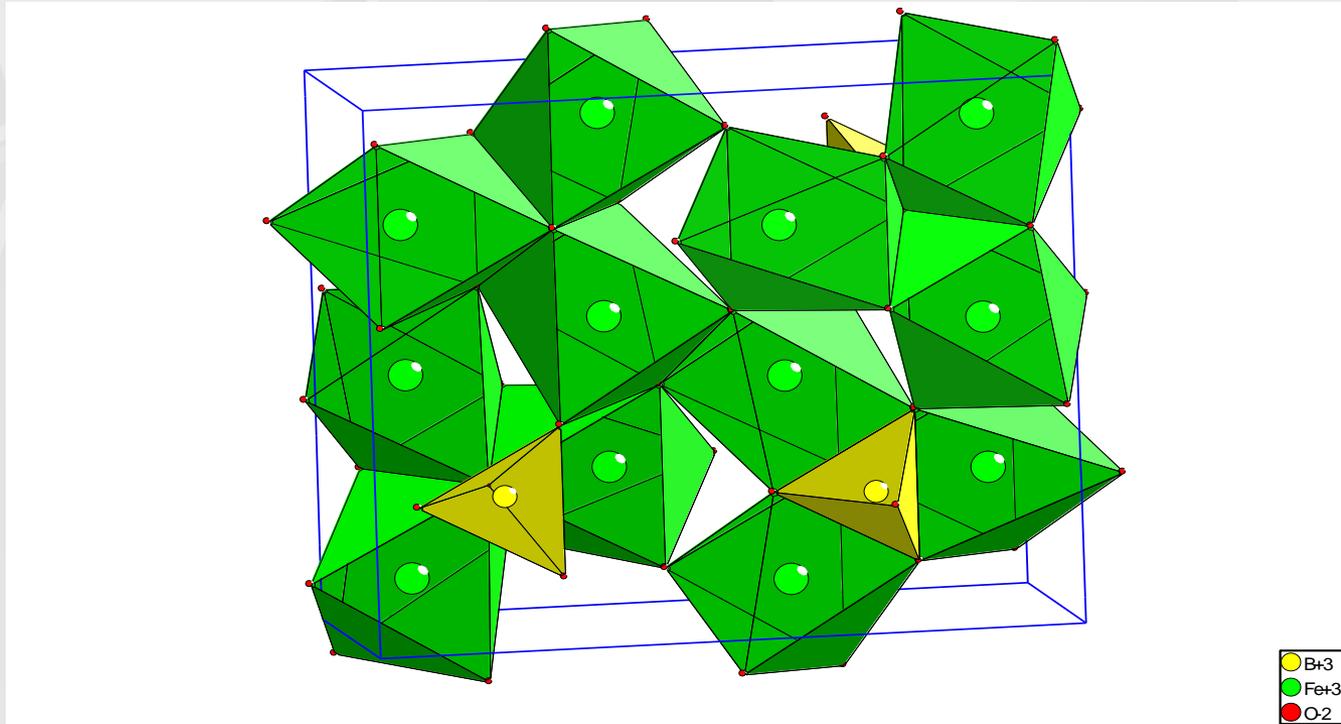
Fig. 1. Energy dependent integrated intensities of the (001) reflection with incident s and p polarization, of YBa₂Cu₃O₇ at the Cu L_{2,3} edges .

Для сигма поляризации хорошо видна интерференция с нерезонансным рассеянием

Из работы: **RESONANT SOFT X-RAY SCATTERING AND ABSORPTION ON YBa₂Cu₃O₇**

U. Staub, V. Scagnoli, T. Ramsvik (PSI), A. Erb (Munich), and J. M. Tonnerre (CNRS-Grenoble)

Резонансная дифракция в ортоборате железа Fe_3BO_6 ($Pnma$)



Fe in two crystallographically nonequivalent positions:
4(c) with local symmetry m and general 8(d).

G. Beutier, E. Ovchinnikova, S.P. Collins, V.E. Dmitrienko, *et al.* Interplay of inequivalent atomic positions in resonant x-ray diffraction of Fe_3BO_6 . *J. Phys.: Condensed Matter*, 2009, Vol. 21 265402.

Сравнение расчетов с экспериментом для Fe_3VO_6

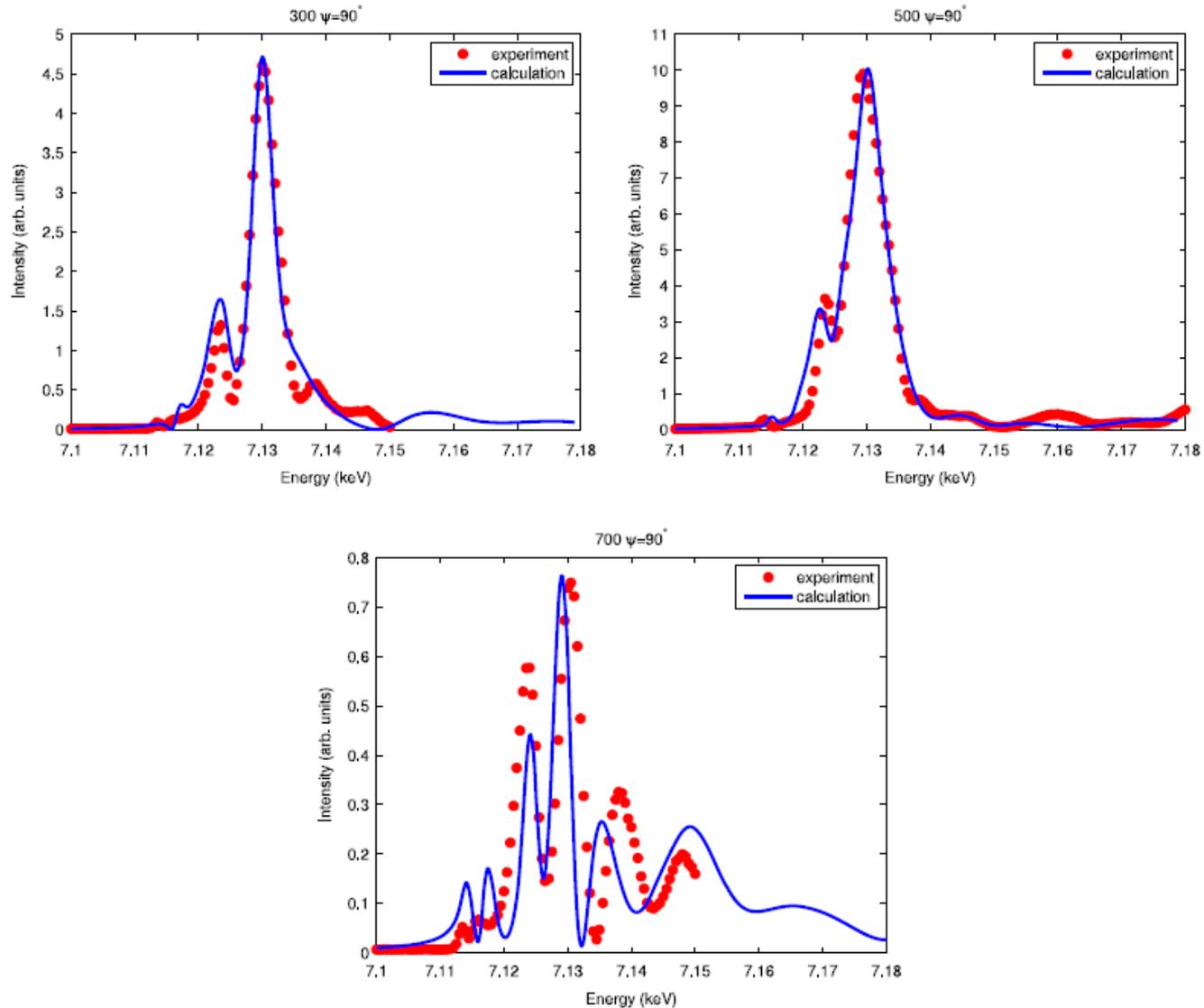


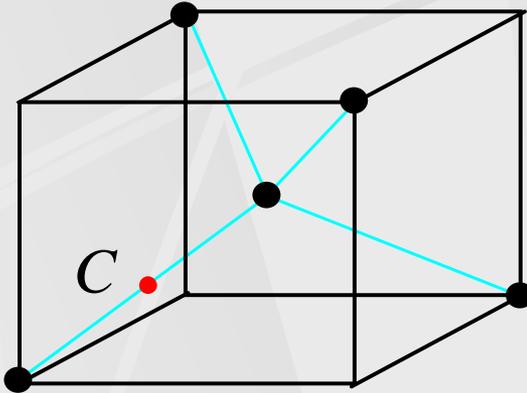
Figure 7. Energy spectra of the reflections 300, 500 and 700 at the azimuth $\psi = 90^\circ$: FDMNES calculations versus experimental data.

Forbidden reflections in Ge

PHYSICAL REVIEW B

VOLUME 49, NUMBER 21

1 JUNE 1994



$$f_{jk}^{dd} \sim \delta_{jk}, F_{jk}^{dd} = 0,$$

$$f_{jkm}^{dq,a} = 0,$$

$$f_{jkm}^{dq,s} = f^{dq,s}(\omega), \text{ if}$$

$$j \neq k, k \neq m, m \neq j$$

Tetrahedral anisotropy of x-ray anomalous scattering

David H. Templeton and Lieselotte K. Templeton

Department of Chemistry, University of California, Berkeley, California 94720

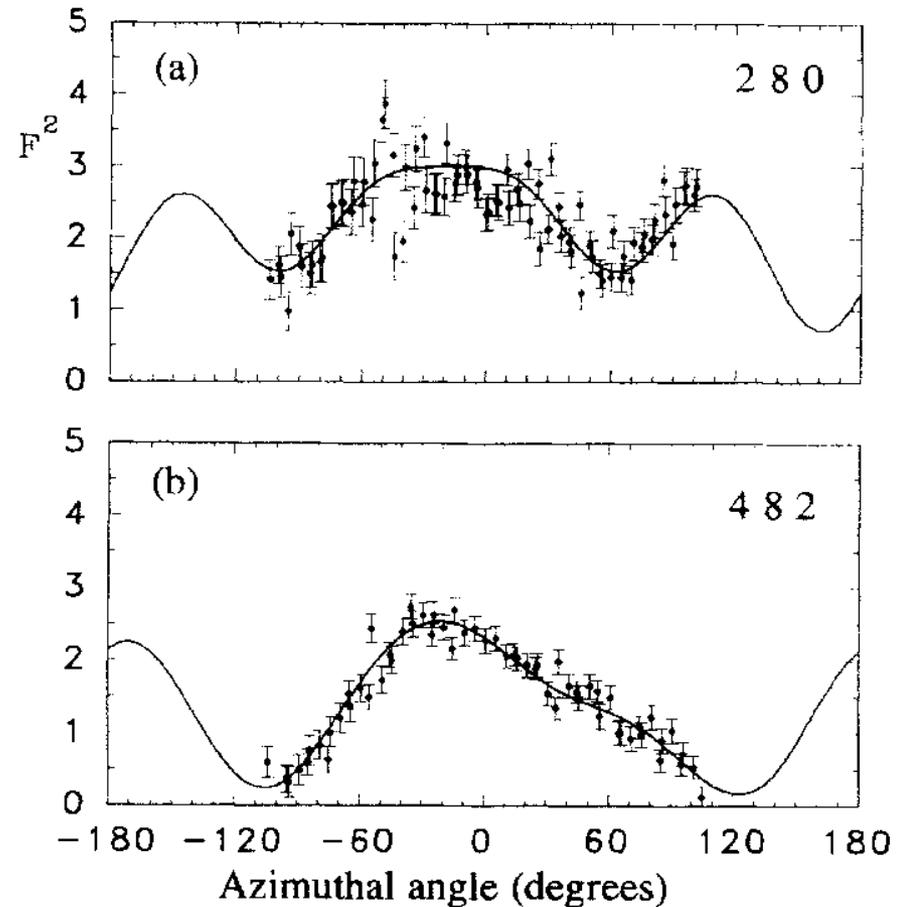
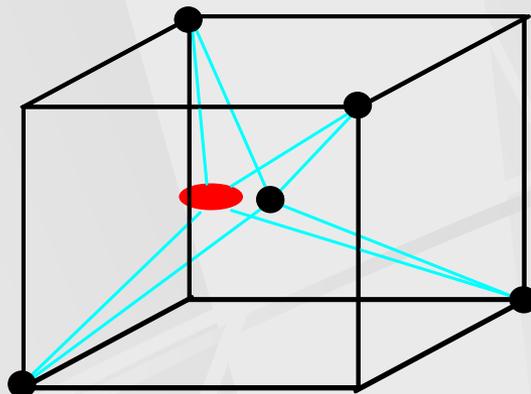


FIG. 5. Observed and calculated variation of intensity with azimuth for reflections of Ge that are forbidden (a) by a glide rule (280) and (b) by structure-factor algebra (482).



Модель смещения одного атома в кристалле Ge

$$F_{jk}(\vec{H}) \approx \sum_s \overline{f_{jk}^s(\vec{0}, \vec{r}_s, \vec{r}_{s1}, \dots)} \exp(i\vec{H}\vec{r}_s)$$

$$F_{jk}(\vec{H}) \approx \sum_s \overline{(f_{jk}^{s,0} + f_{jkm}^{s,dd} u_m) (+i\vec{H}\vec{r}_s + \dots)} \exp(i\vec{H}\vec{r}_s)$$

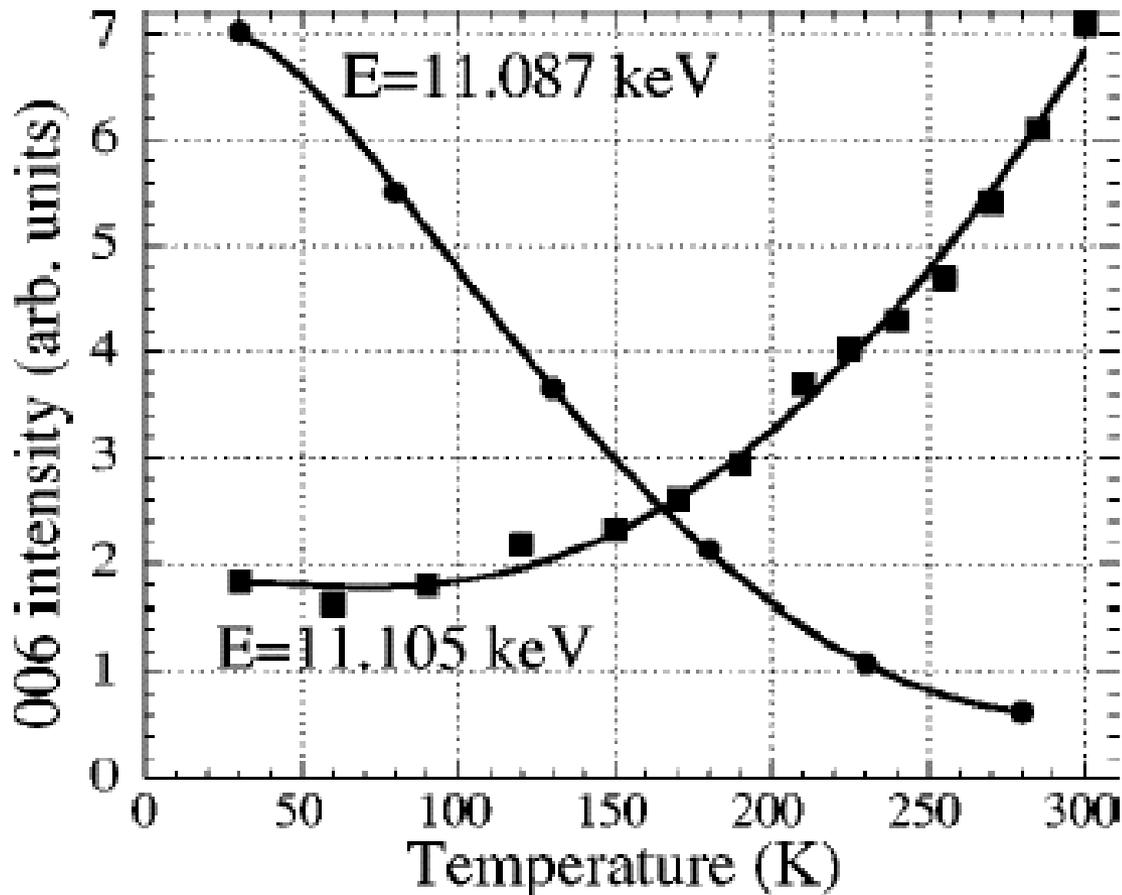
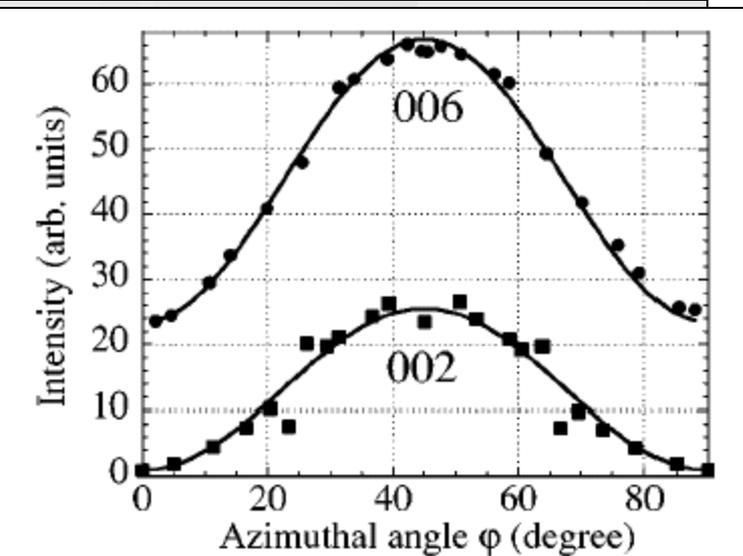
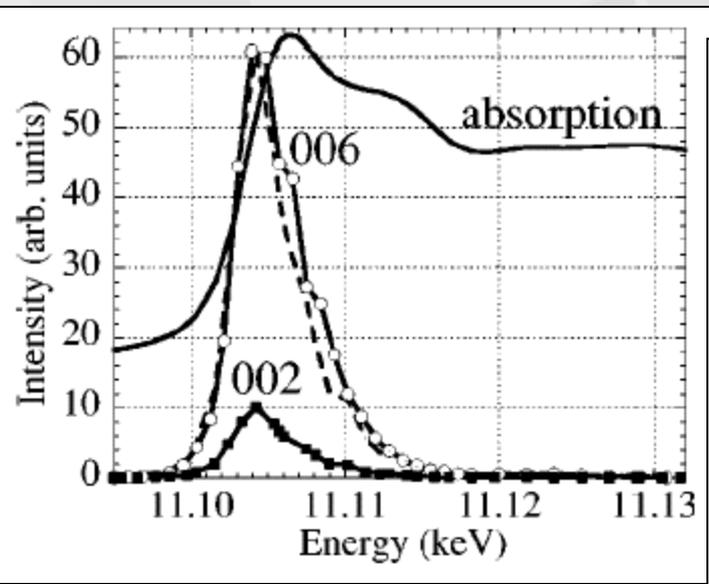
$$F_{jk}^{TMI}(\vec{H}) \approx \sum_s \overline{if_{jkm}^s H_l u_m^s u_l^s} \exp(i\vec{H}\vec{r}_s)$$

$$F_{ij}(\vec{q}, k+l=4n+2) \approx f_{ij}^1 - f_{ij}^2 \neq 0 \quad f_{ijk}^1 = -f_{ijk}^2$$

$$F_{jk}^{TMI}(\vec{q}, k+l=4n+2) \approx \frac{16}{3} \pi i f u^2 \begin{pmatrix} 0 & l & k \\ l & 0 & 0 \\ k & 0 & 0 \end{pmatrix} \quad \overline{u^2} \approx \frac{h}{2M\Omega} \text{cth} \left(\frac{h\Omega}{k_B T} \right)$$

Spectral, azimuthal and temperature dependences observed for the 002 and 006 thermal-motion-induced (TMI) reflections in Ge

J.Kokubun, M.Kanazawa, K.Ishida, V.E.Dmitrienko. Phys. Rev. B, **64**, 073203 (2001).



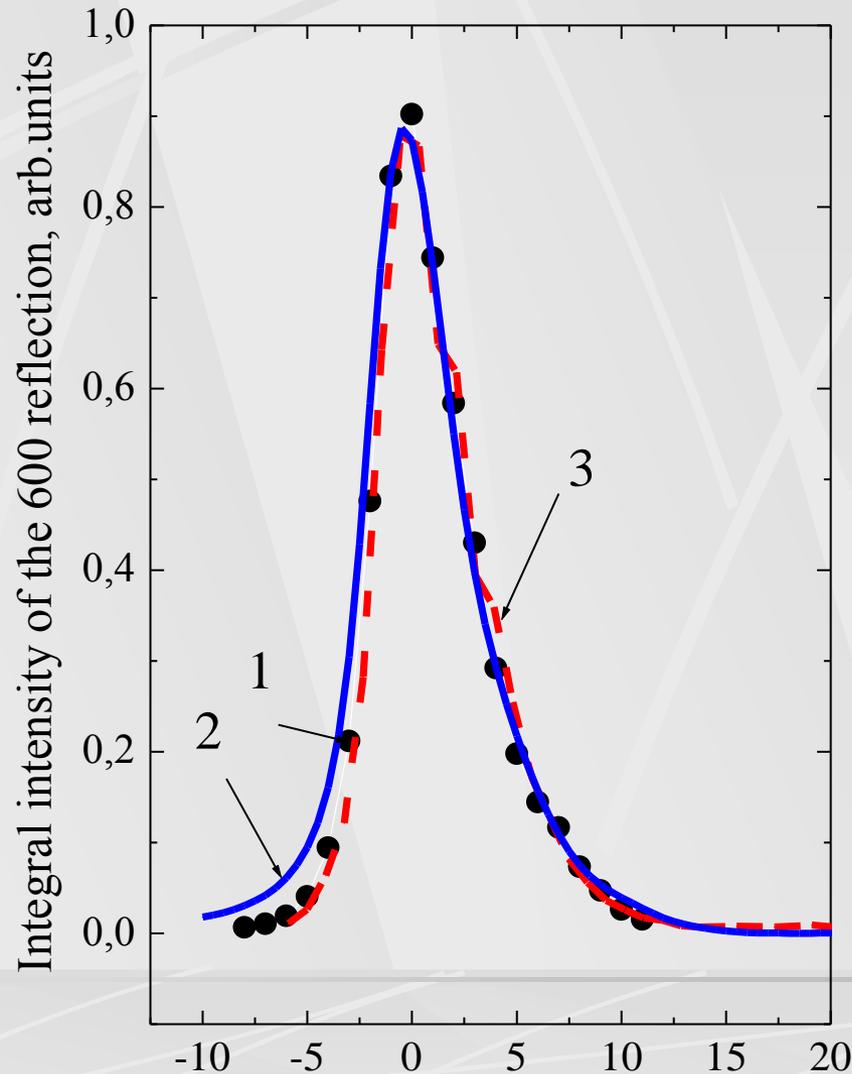
Измерение на КИСИ

Э.Х. Мухамеджанов, М.М. Борисов, А.Н. Морковин, 2007

**1- the 006
reflection
measured at the
Synchrotron in
RSC “Kurchatov
Institute”,**

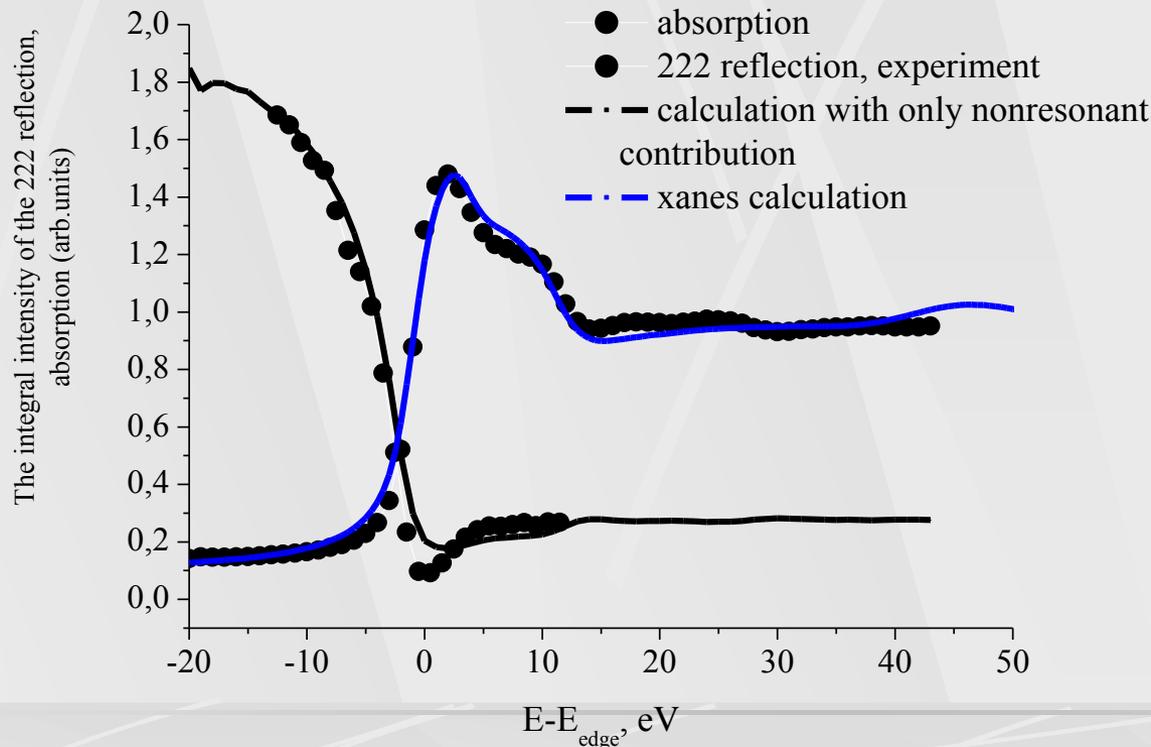
**2 – fitting with dq
and Thermal-
Motion-Induced
terms**

**3 – experiment,
made at the
Photon Factory in
Tsukube**



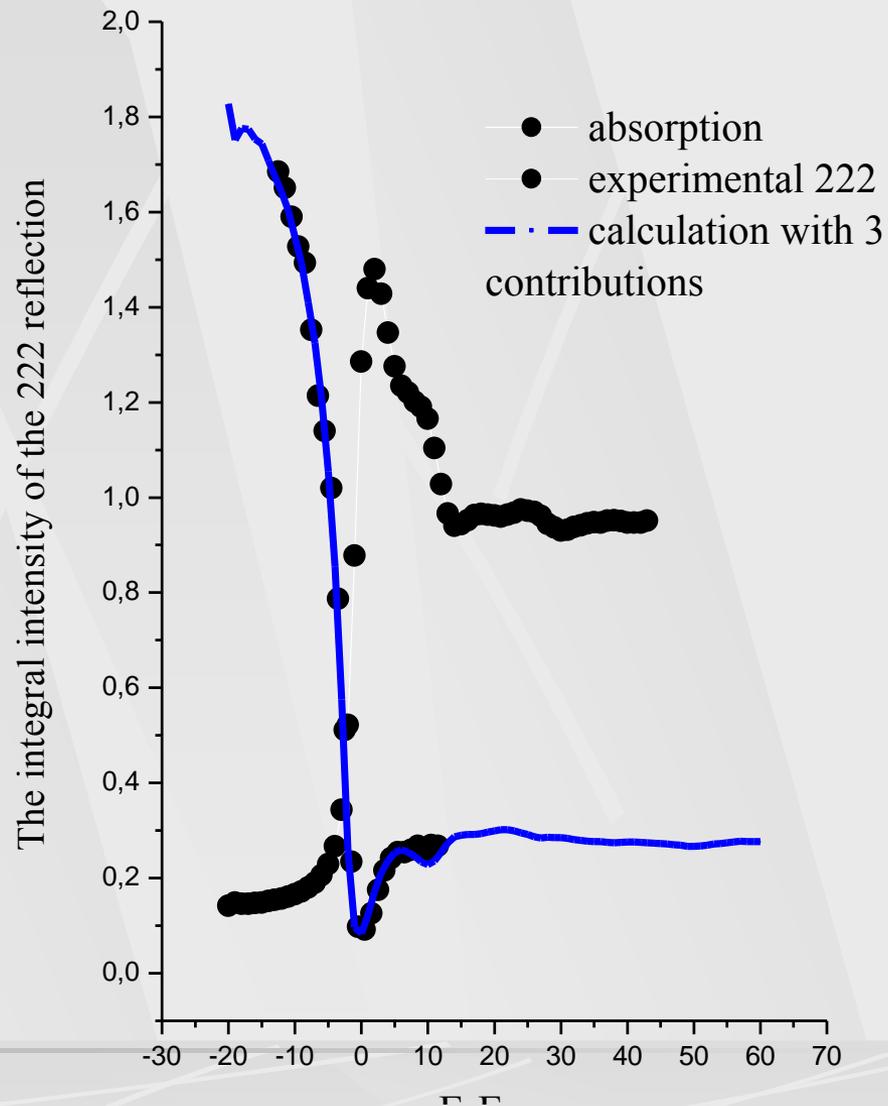
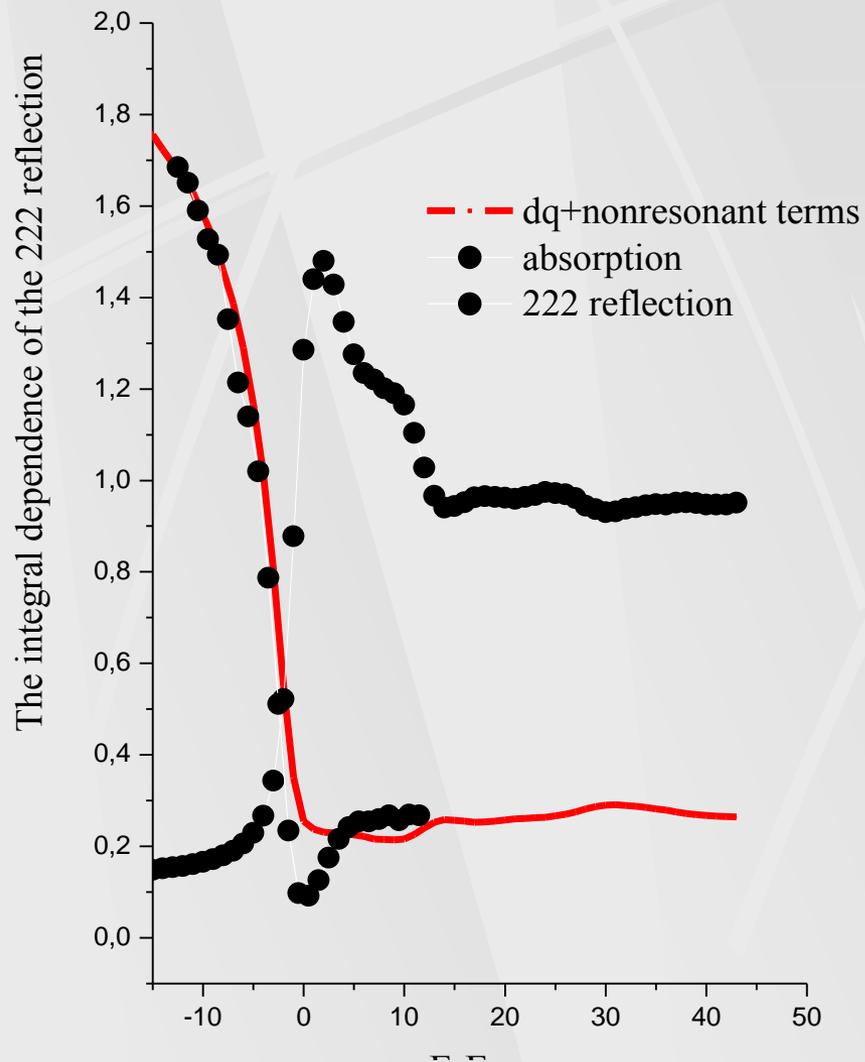
Измерение фазы запрещенных рефлексов в Ge: интерференция между резонансным и уже известным нерезонансным вкладами в рефлекс 222

$$I(hkl) \sim \frac{|F(hkl)|^2}{\mu(E)} \quad F(222) = F_0 + F_{ij}^{dq} + F_{ij}^{TMI}$$

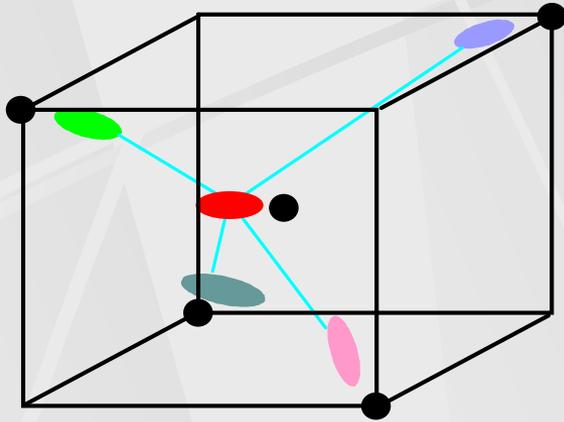


$$F_0(222) = +1.02 \text{ el.}$$

J.R.Roberto,
B.W.Batterman,
D.T.Keating, Phys.
Rev. B 9,2590 (1974).



Displacement of all atoms in Ge



Phenomenological approach:

$$f_{jk} \approx \sum_N f_{jkm} u_m + \dots$$

$$F_{ij} \approx \frac{16}{3} i \left[f_{xyx} - f_{xyz} \right] u_{\perp}^2 + u_{\parallel}^2 \left[f_{xyx} + f_{xyz} \right] T_{ikn} H_n \exp\left(-\frac{\overline{Hu}^2}{2}\right)$$

Fitting of the experimental data and simulations 

Рефлекс 006 во всем интервале температур

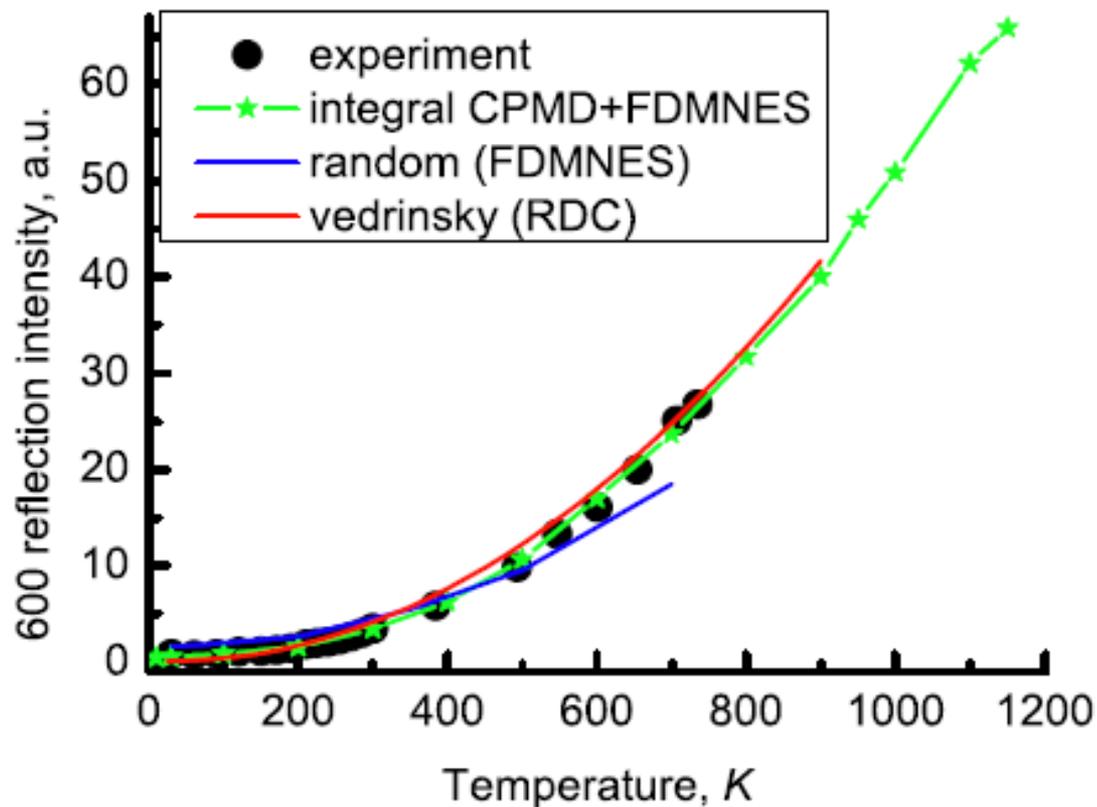
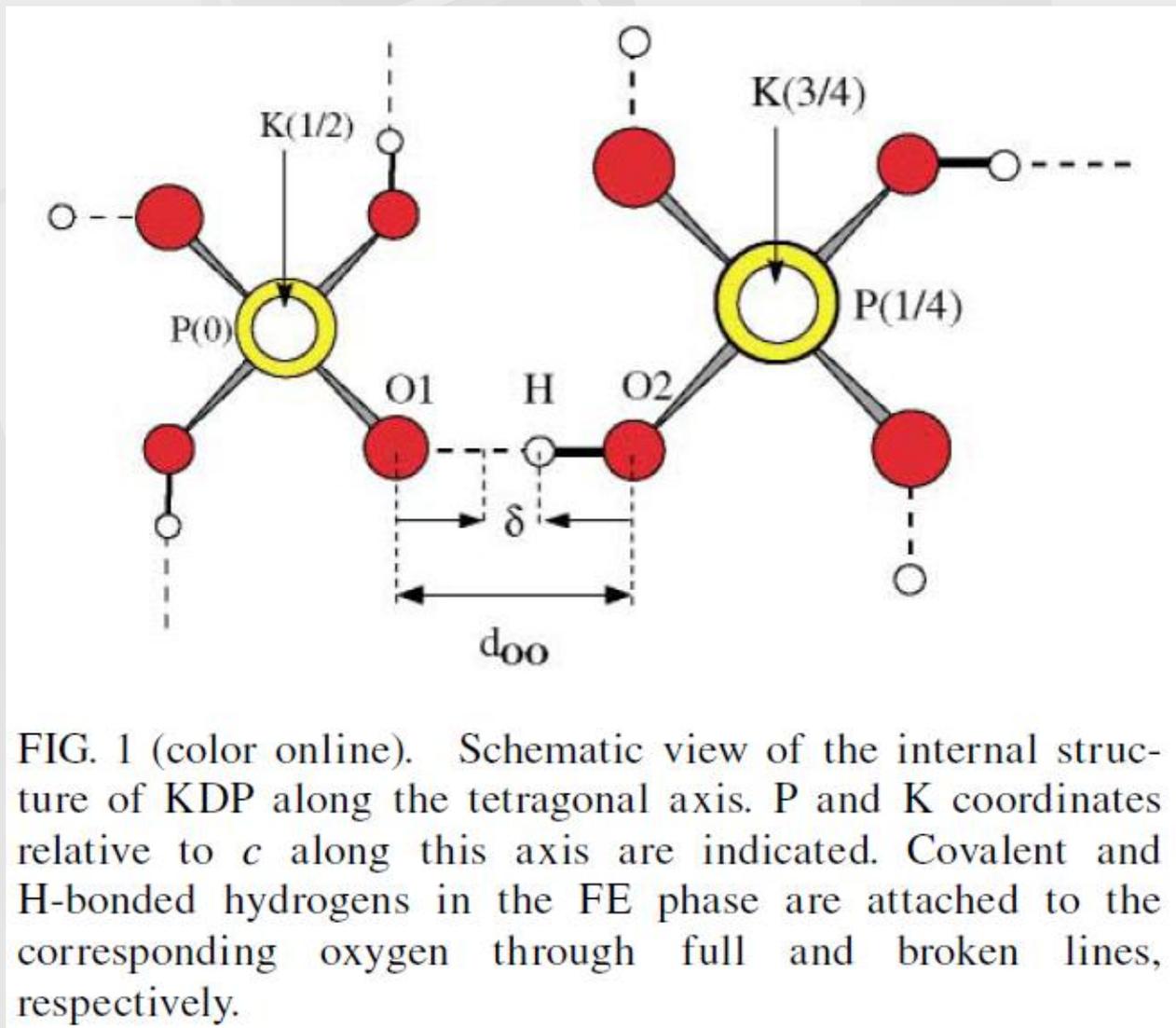


FIG. 6: (Color online) Temperature dependence of intensity: simulation and experiment

Атомная структура KH_2PO_4



Атомы калия в точках с симметрией $\bar{4}$, нарушаемой скачками водорода

Crystal structure of KH_2PO_4

Space groups:

high temperature ($T > 123\text{K}$) $I\bar{4}2d$ (No. 122);

symmetry of K positions is $\bar{4}$,
no **dipole-dipole** contribution to pure resonant reflection;

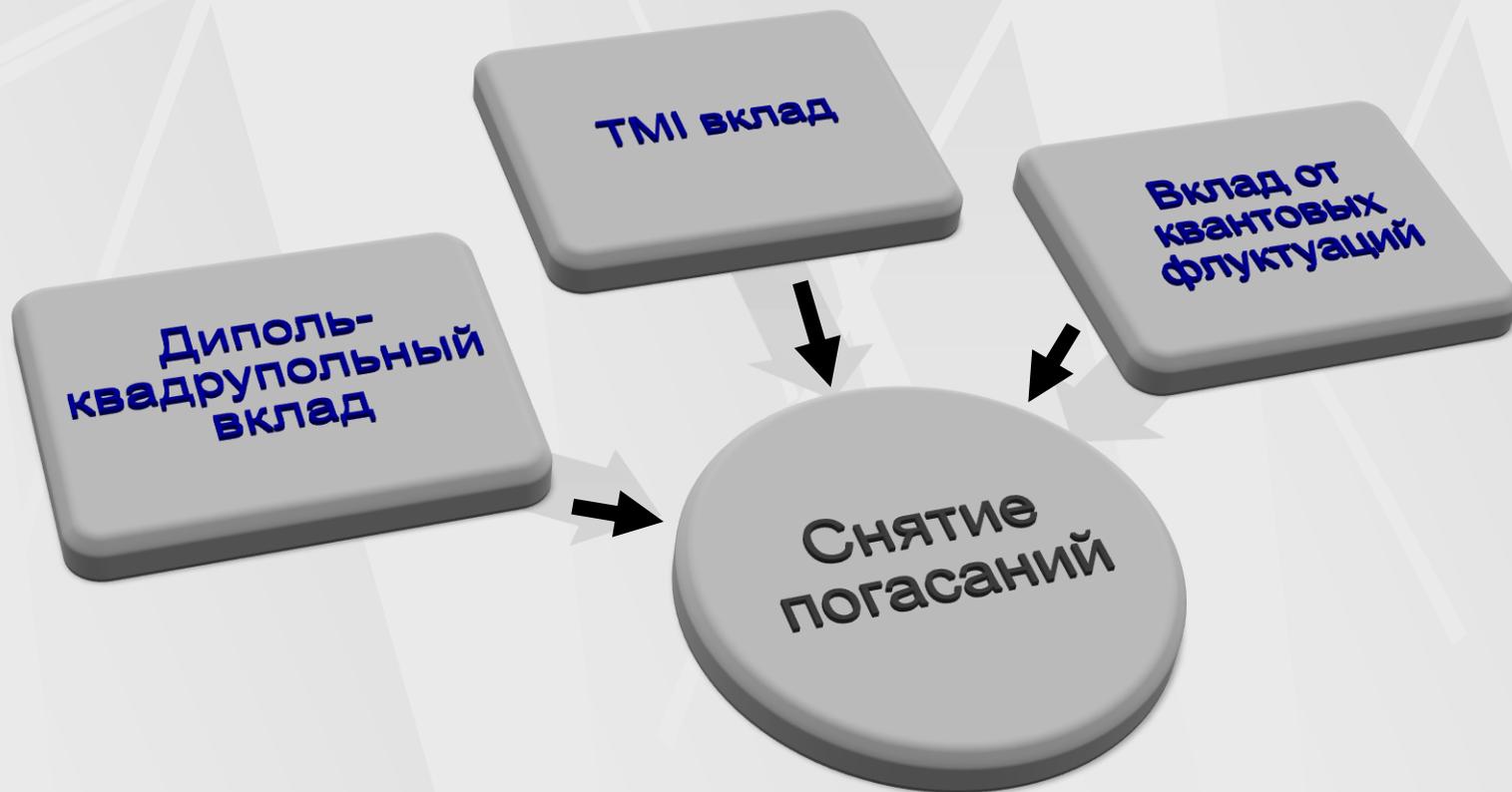
low temperature ($T < 123\text{K}$) $Fdd2$ (No. 43);

ferroelectric;

symmetry of K positions is $..2$;

the main contribution is **dipole-dipole**, it is proportional to the order parameter, i.e. $(T_c - T)^{0.5}$

Вклады в запрещенные рефлексы в высокотемпературной фазе



Диполь-квадрупольный вклад

элементы симметрии атомных позиций: инверсионная ось -4 и ось 2

Инвариантность: $XYZ \rightarrow Y-X-Z \rightarrow -X-YZ \rightarrow -YX-Z$
Связь между атомами: $XYZ \rightarrow Y+1/2, X, Z+3/4$

Структурная амплитуда:

$$F^{dq}(\mathbf{H}, \mathbf{l}) = \begin{pmatrix} f_{xxz}^s H_z & 0 & f_{xzx}^s H_x + f_{xzx}^a l_x \\ 0 & -f_{xxz}^s H_z & -f_{xzx}^s H_y - f_{xzx}^a l_y \\ f_{xzx}^s H_x - f_{xzx}^a l_x & -f_{xzx}^s H_y + f_{xzx}^a l_y & 0 \end{pmatrix}$$

- Отражения запрещены в диполь-дипольном приближении,
- но они возникают в диполь-квадрупольном приближении.

$$\mathbf{l} = \mathbf{k} + \mathbf{k}', \quad \mathbf{H} = \mathbf{k}' - \mathbf{k},$$

s и a - симметричная и антисимметричная части соответствующей тензорной компоненты.

Термоиндуцированный вклад

тепловые колебания всех атомов

$F^{dd} \rightarrow F'^{dd}$ (тензорные атомные факторы)

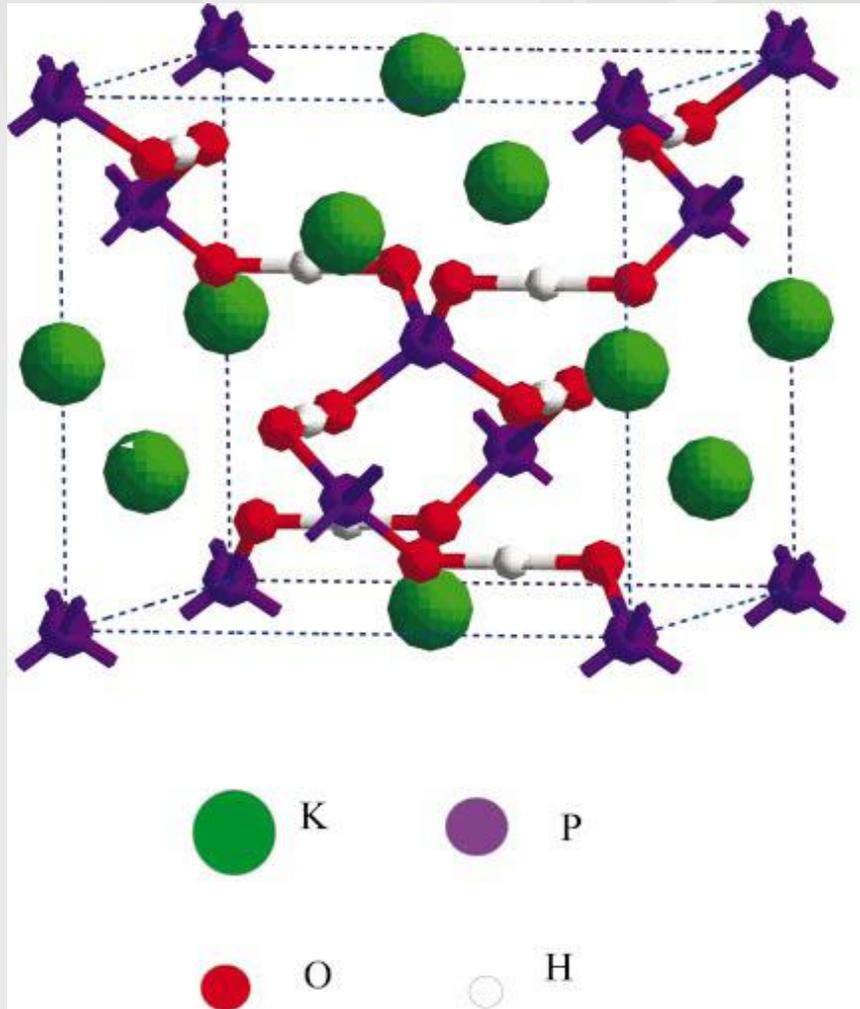
$$F^{TMI} \sim \overline{u^2}$$

$$\overline{u^2} \sim T$$

$$F^{TMI}(\mathbf{H}) = 2\pi i \begin{pmatrix} \frac{\partial f_{xx}^{dd}}{\partial z} H_z \overline{u_z^2} & 0 & \frac{\partial f_{xz}^{dd}}{\partial x} H_x \overline{u_x^2} \\ 0 & -\frac{\partial f_{xx}^{dd}}{\partial z} H_z \overline{u_z^2} & -\frac{\partial f_{xz}^{dd}}{\partial x} H_x \overline{u_x^2} \\ \frac{\partial f_{xz}^{dd}}{\partial x} H_x \overline{u_x^2} & -\frac{\partial f_{xz}^{dd}}{\partial x} H_x \overline{u_x^2} & 0 \end{pmatrix}$$

Необходимо учитывать термоиндуцированный вклад

Вклад от прыжков водорода

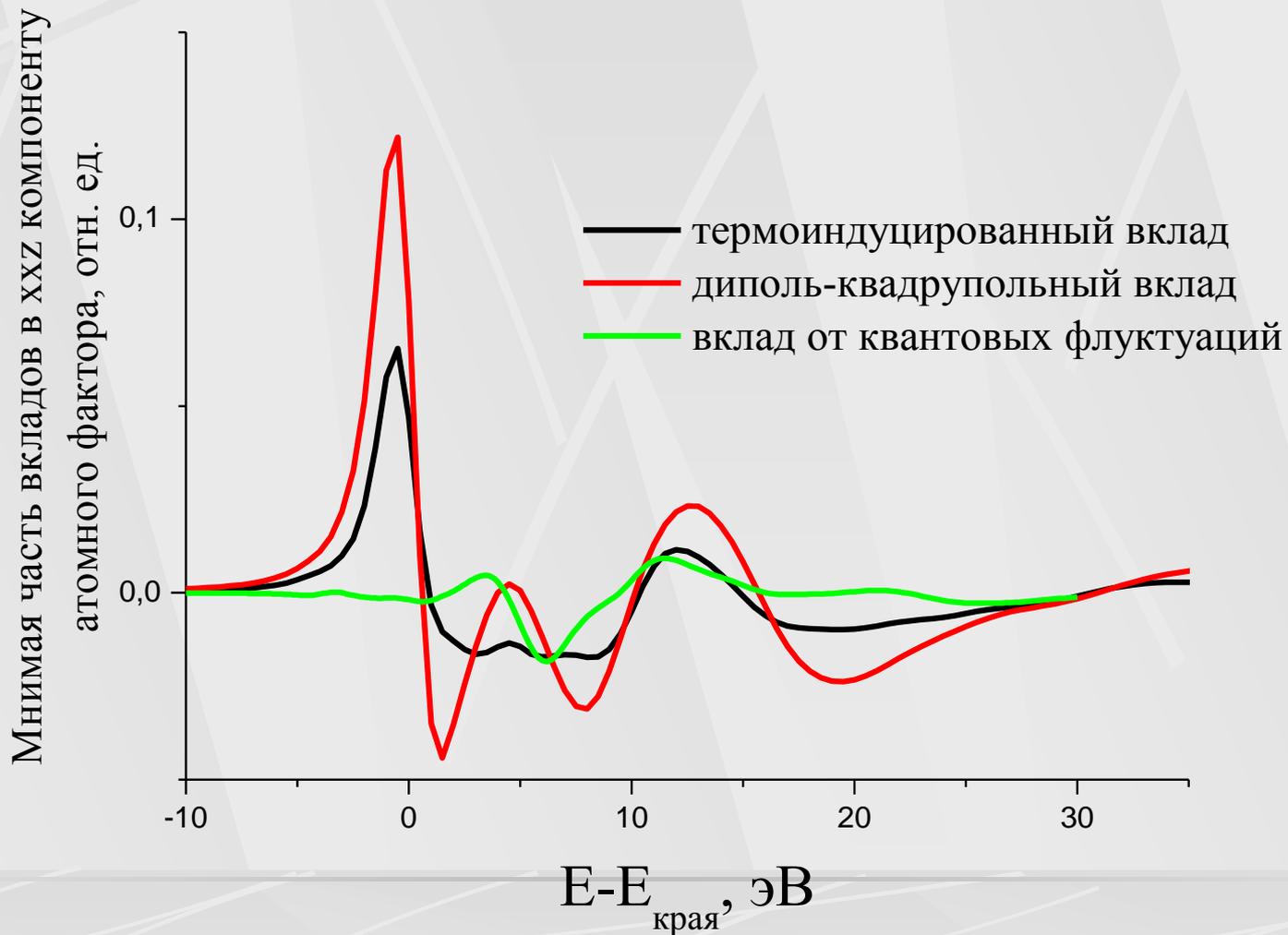


Структура KDP

$$F^j(\mathbf{H}) = \sum_s \Delta f_{ij,s}^{dd} u_s \exp(2\pi i \mathbf{H} r_s^0)$$

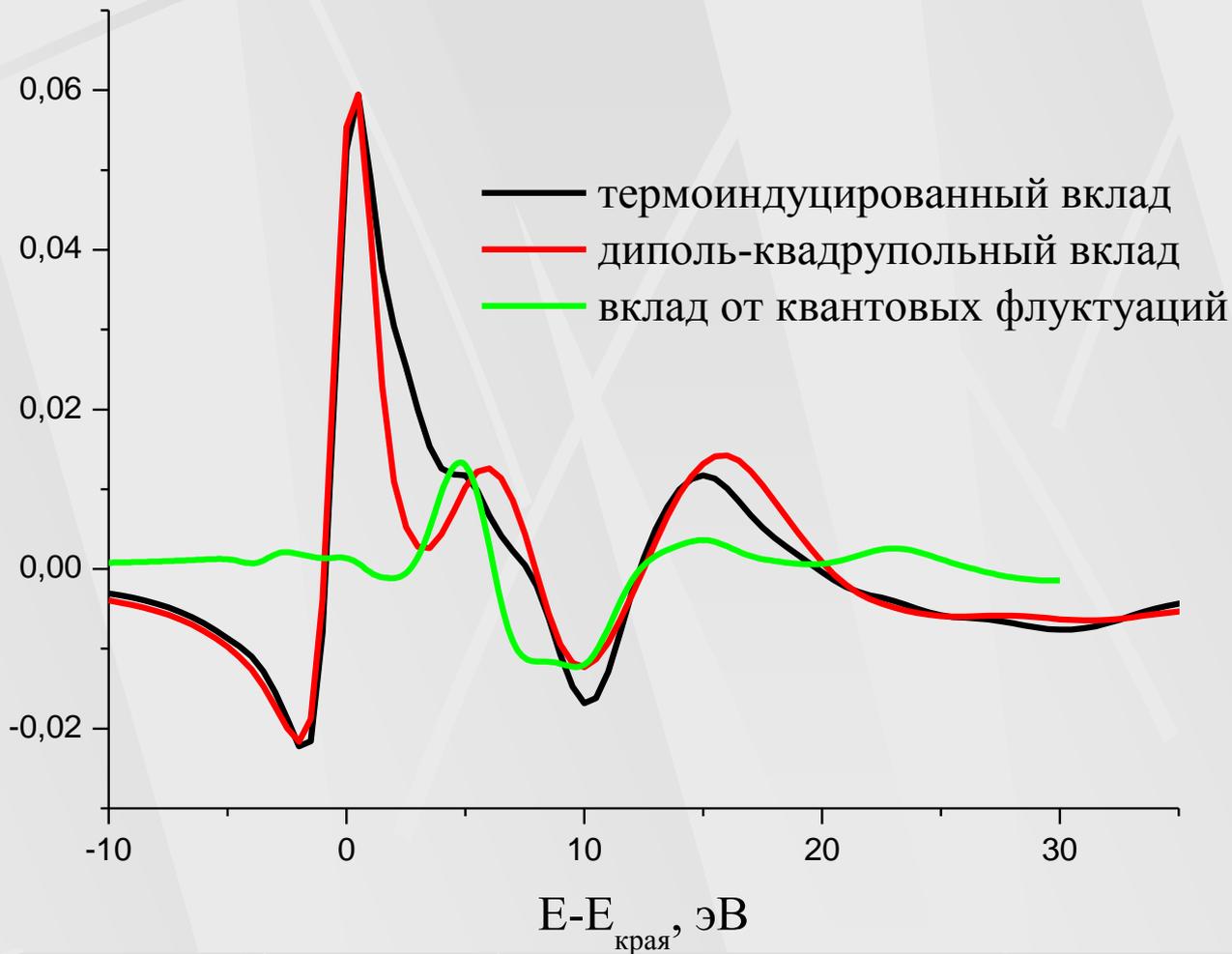
В высокотемпературной фазе атомы водорода совершают квантовые и/или тепловые перескоки в потенциальной яме с двумя минимумами, что является причиной дополнительной локальной анизотропии окружения рубидия.

Вклады в атомный фактор



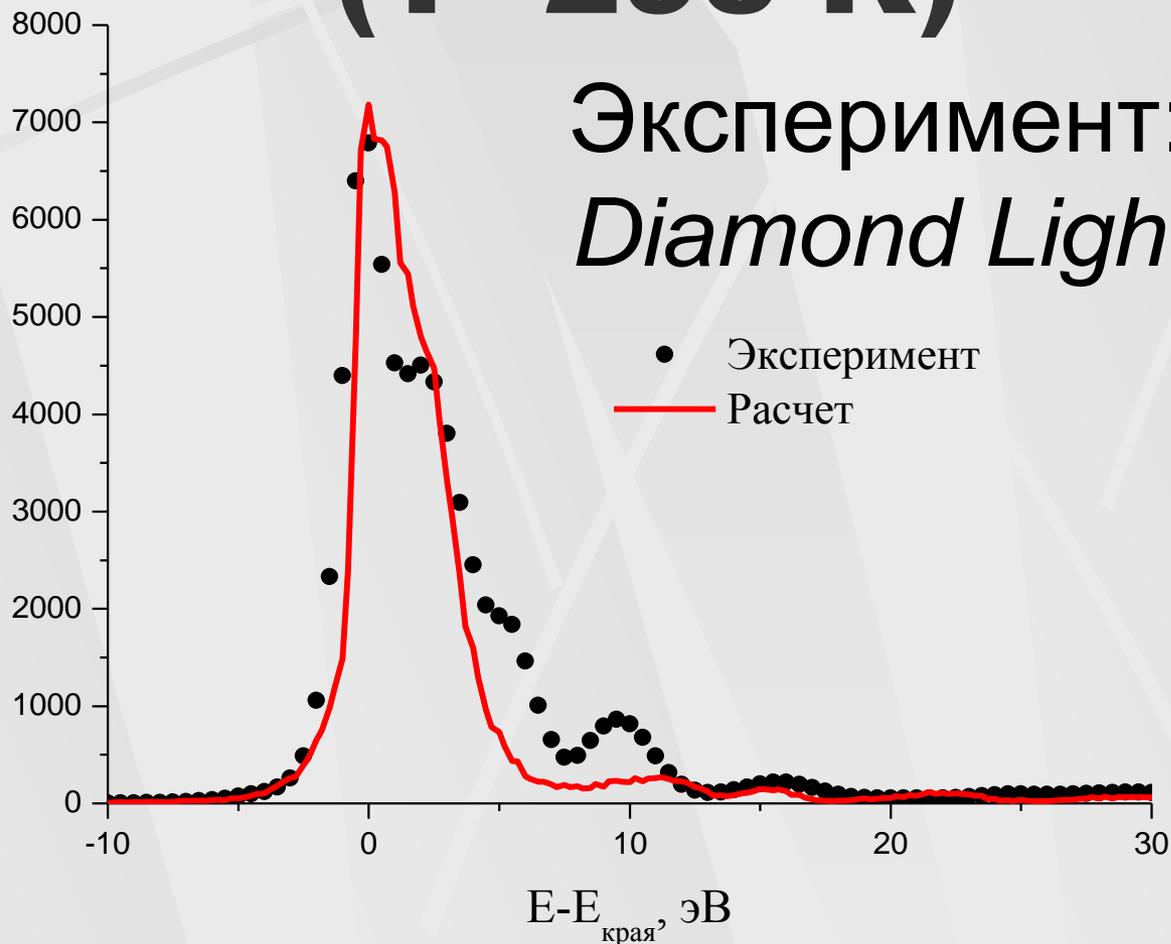
Вклады в атомный фактор

Реальная часть вкладов в XX компоненту
атомного фактора, отн. ед.



Рефлекс 002 в high-KDP ($T=293\text{ K}$)

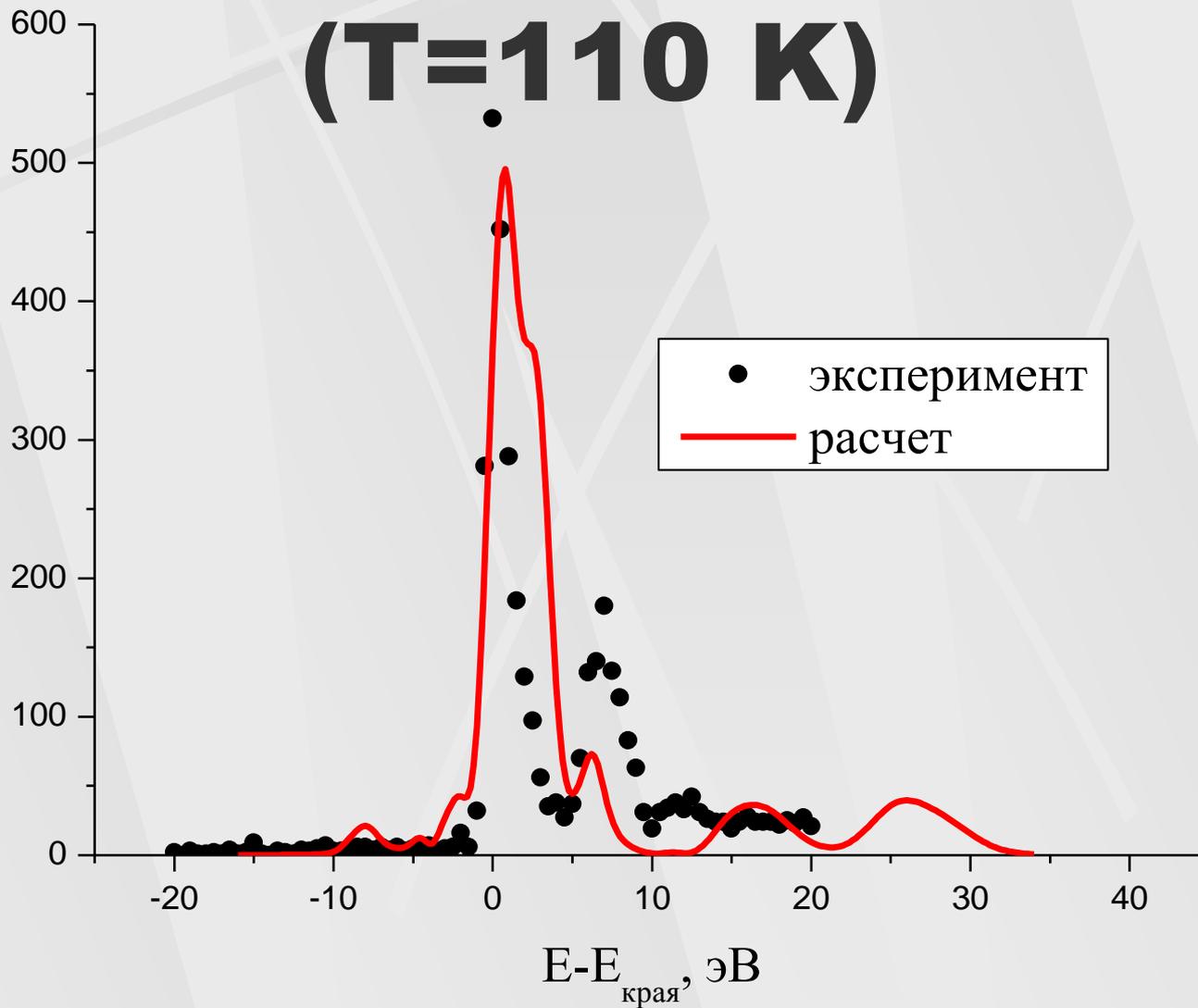
Интегральная интенсивность отражения
002 в высокотемпературной фазе, отн. ед.



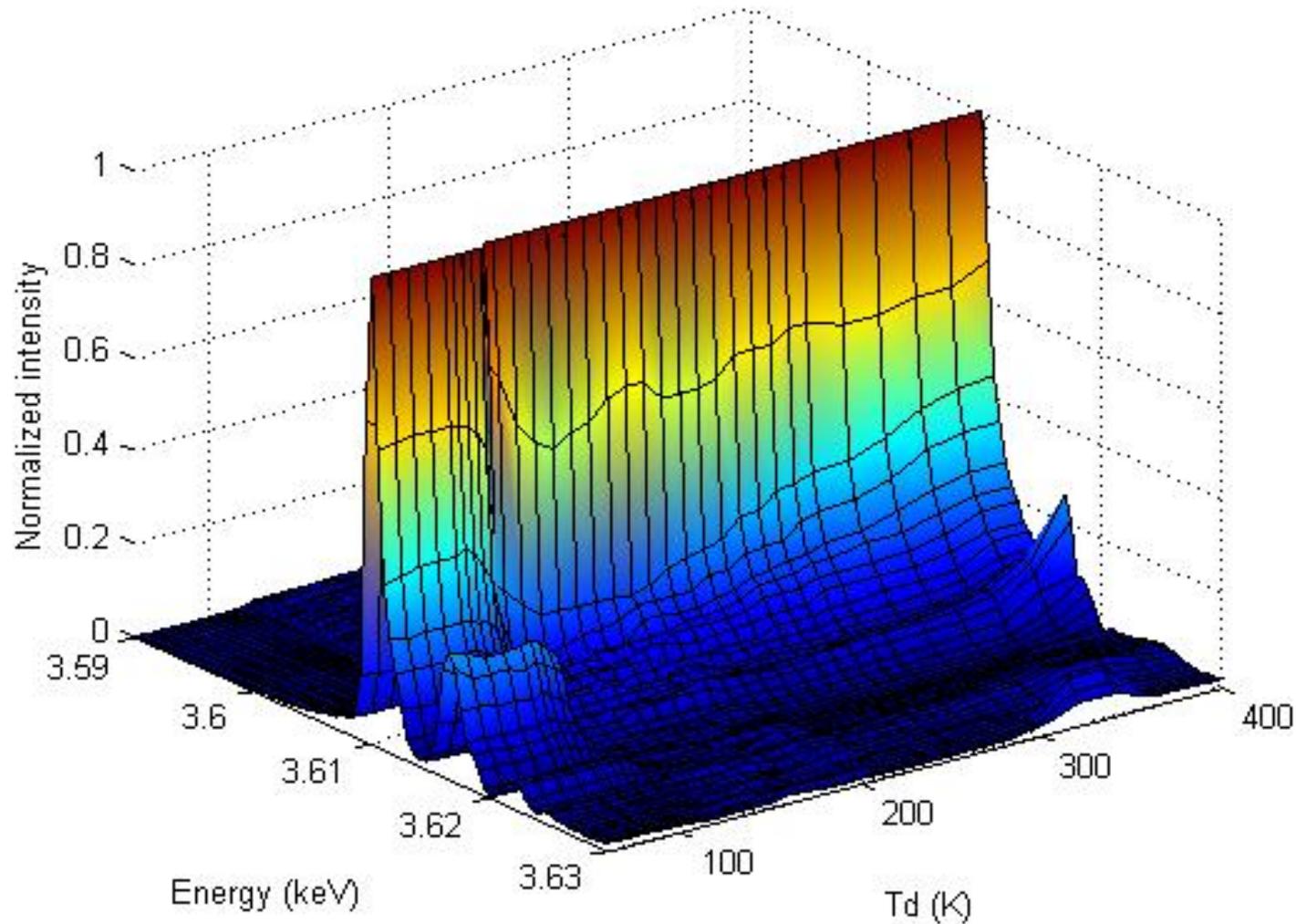
Для RbH_2PO_4 запрещенные рефлексы изучались в КИСИ

Рефлекс 002 в low-KDP ($T=110$ К)

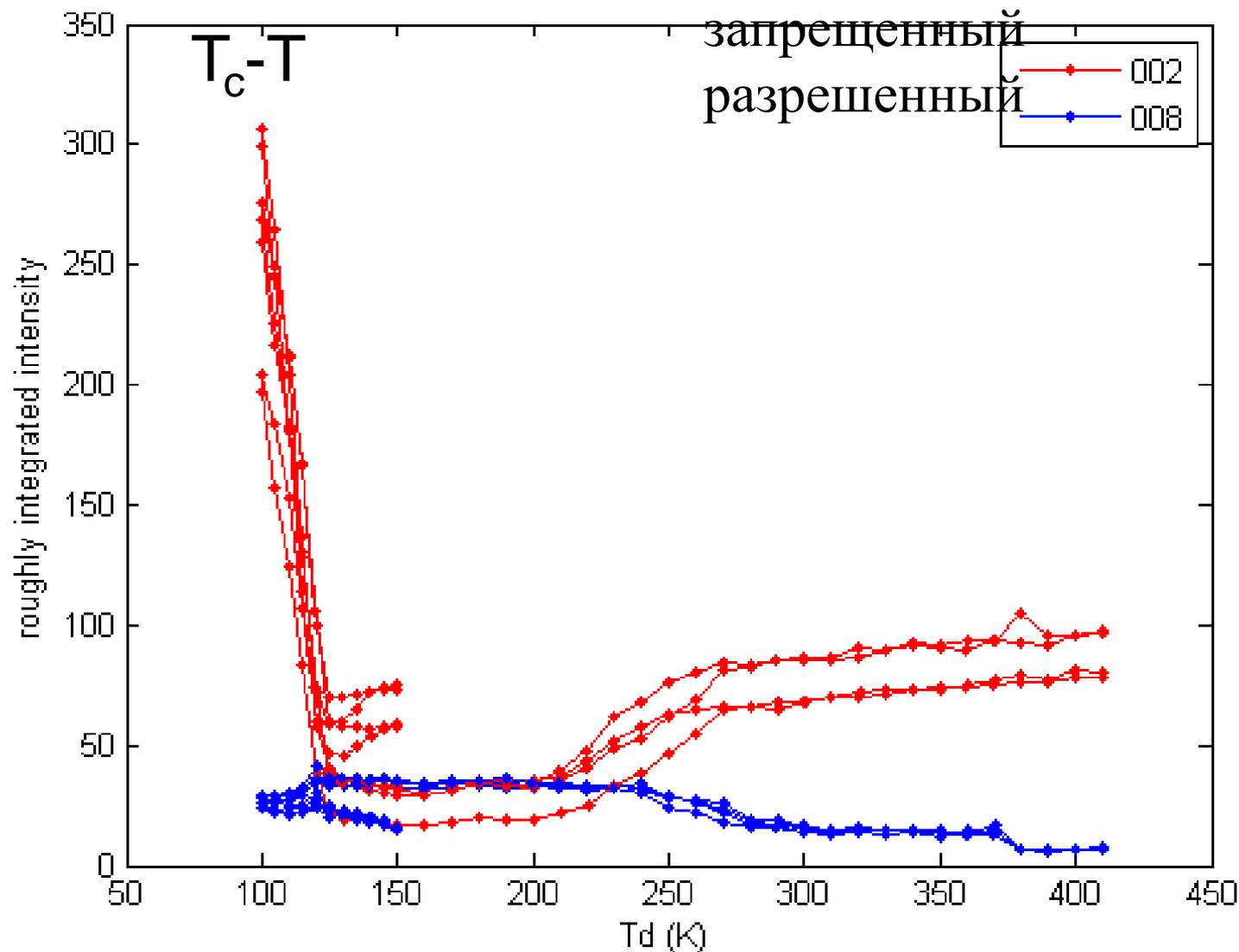
Интегральная интенсивность отражения
002 в низкотемпературной фазе, отн. ед.



Temperature dependence of the energy spectra of the 002 forbidden reflection of KDP at the Potassium *K*-edge. The intensity has been normalized to the peak of the spectra, evidencing the change of line shape. The phase transition at 123 K is clearly visible.



Температурную зависимость описать не удаётся!



Пространственные группы, допускающие существование естественного кругового дихроизма

Нецентросимметричные группы симметрии	Обозначения Шенфлиса	Псевдо-скаляр	Полярный вектор	Псевдо-девиатор
		Энантиоморфизм E1.M1	Voigt/Fedorov OA E1.M1+E1.E2	XNCD E1.M1+E1.E2
$\bar{4}3m; \bar{6}m2; \bar{6}$	$T_d; D_{3h}; C_{3h}$	No	No	No
432; 23	O; T	Yes	No	No
622 ; 32 422	$D_6; D_3; D_4$	Yes	No	Yes
6mm; 4mm; 3m	$C_{6v}; C_{4v}; C_{3v}$	No	Yes	No
6 ; 3; 4	$C_6; C_3; C_4$	Yes	Yes	Yes
$\bar{4}2m$	D_{2d}	No	No	Yes
$\bar{4}$	S_4	No	No	Yes
mm2	C_{2v}	No	Yes	Yes
222	D_2	Yes	No	Yes
2	C_2	Yes	Yes	Yes
m	C_s	No	Yes	Yes
1	C_1	Yes	Yes	Yes

Vector part of optical activity in ZnO?

Table: Irreducible parts of optical activity (antisymmetric third-rank tensor)

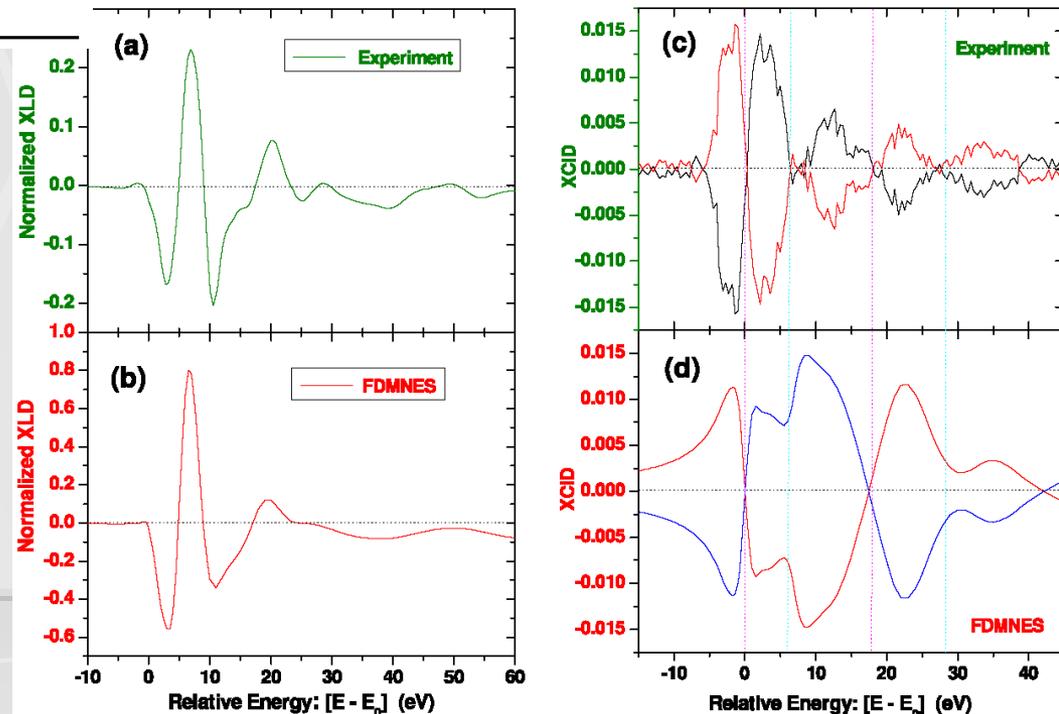
Crystal classes	Point groups	Irreducible parts of optical activity		
		Pseudo-scalar Enantiomorphism	Polar vector Voigt/Fedorov	Pseudo-deviator XNCD
$\bar{4}3m$ $\bar{6}m2$ $\bar{6}$	T_d D_{3h} C_{3h}	-	-	-
432 23	O T	+	-	-
622 32 422	D_6 D_3 D_4	+	-	+
$6mm$ $3m$ $4mm$	C_{6v} C_{3v} C_{4v}	-	+	-
6 3 4	C_6 C_3 C_4	+	+	+
$\bar{4}2m$	D_{2d}	-	-	+
$\bar{4}$	S_4	-	-	+
$mm2$	C_{2v}	-	+	+
222	D_2	+	-	+
2	C_2	+	+	+
m	C_s	-	+	+
1	C_1	+	+	+

J. Goulon, N. Jaouen, A. Rogalev, *et al.*

Vector part of optical activity probed with x-rays in hexagonal ZnO.

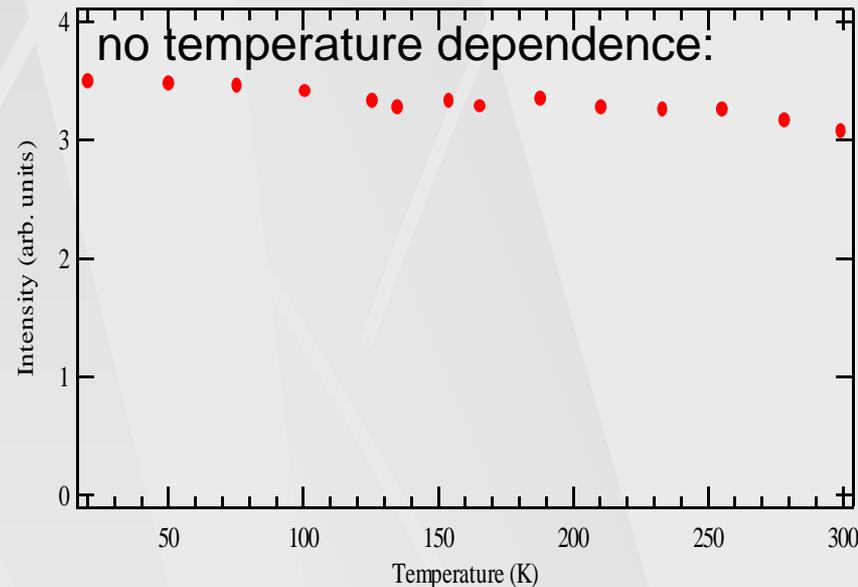
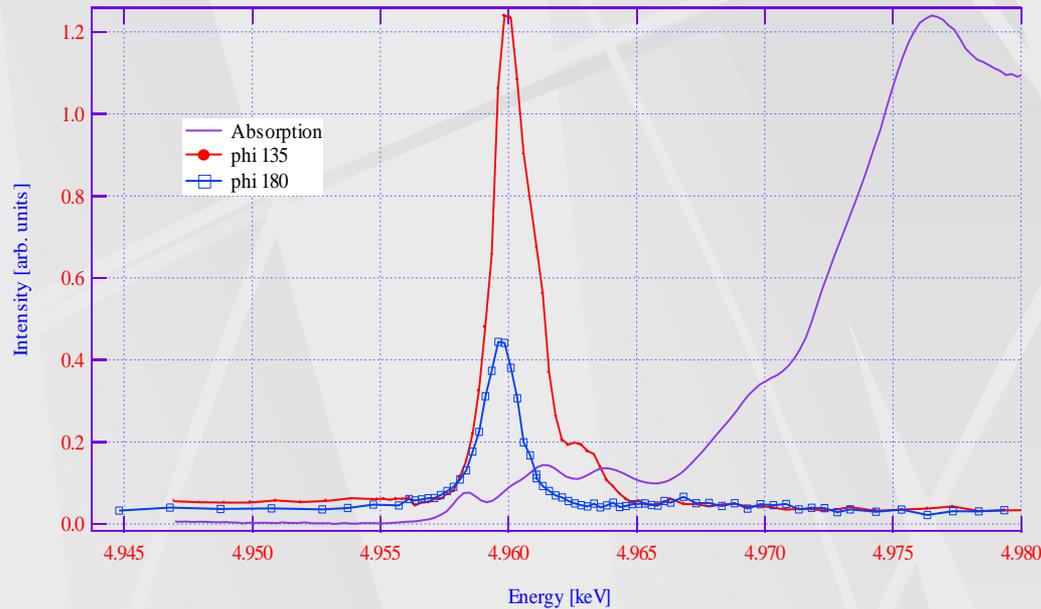
J. Phys.: Condens. Matter. (2007). **19**. 156201.

Figure: Comparison of the measured (a) and simulated with the FDMNES code (b) spectra of the X-ray Linear Dichroism (XLD); both spectra were normalized with respect to the edge jump. Similarly, the measured X-ray Circular Intensity Differentials (XCID) spectra (c) are compared with XCID spectra calculated with FDMNES (d). All simulations were performed with the multiple scattering option of the FDMNES code.



Dipole-quadrupole reflections in anatase, TiO₂

J.Kokubun, K.Ishida, *et al.*



The $\bar{4}m2$ symmetry constrains the dipole-quadrupole terms:

$$f_{\ell jk}^{dqs} = \begin{pmatrix} & xx & yy & zz & yz & zx & xy \\ x & 0 & 0 & 0 & 0 & f_{xzX}^{dqs} & 0 \\ y & 0 & 0 & 0 & -f_{xzX}^{dqs} & 0 & 0 \\ z & f_{zXx}^{dqs} & -f_{zXx}^{dqs} & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$f_{\ell jk}^{dqa} = \begin{pmatrix} & yz & zx & xy \\ x & 0 & f_{xzX}^{dqa} & 0 \\ y & f_{xzX}^{dqa} & 0 & 0 \\ z & 0 & 0 & 0 \end{pmatrix}.$$

Forbidden reflections in anatase are caused by a hybridization of p and d electronic states with opposite parity.

Dipole-quadrupole reflections in anatase, TiO_2

Simulations made by
Vedrinskii at al., Rostov
University

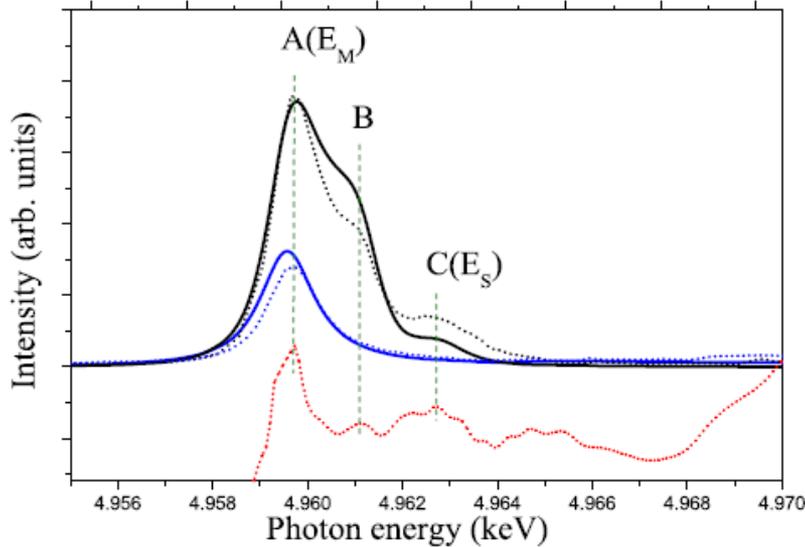


FIG. 8. (Color online) Calculated 002 reflection intensities (solid lines) and experimental data (dotted curves) corrected for absorption (blue for $\varphi=0$, black for $\varphi=\pi/4$). The red curve representing the experimental Ti K-edge absorption spectrum was recorded in fluorescence mode, i.e., simultaneously with the reflection spectra; it shows clearly coincidence between peaks in resonant diffraction and fluorescence.

PHYSICAL REVIEW B 82, 205206 (2010)

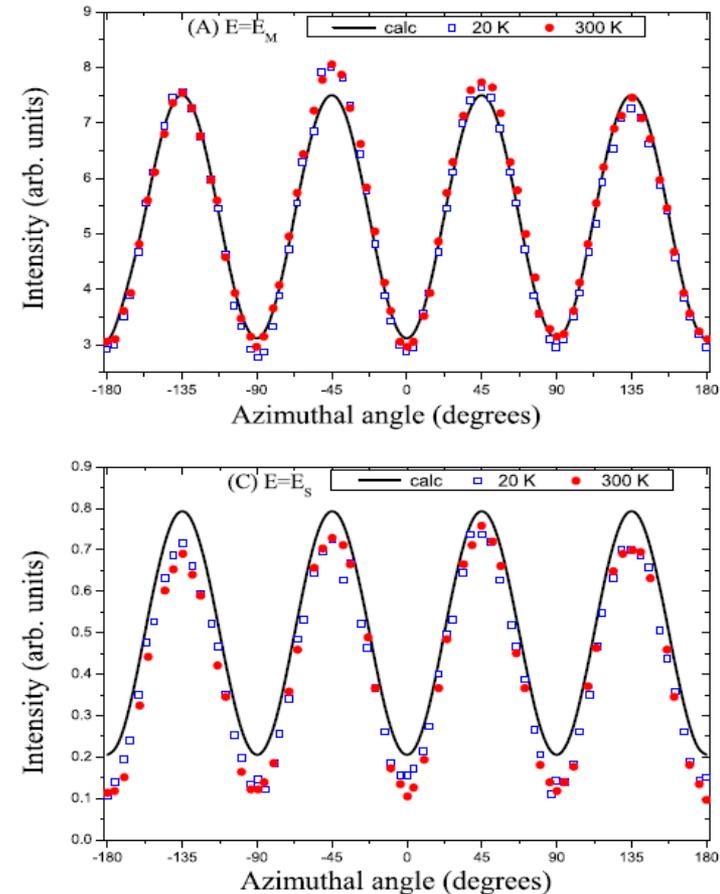


FIG. 2. (Color online) Azimuthal angular intensity dependence of the forbidden reflection 002: (a) at the main resonance peak energy E_M and (b) at the subresonance peak energy E_S (see Figs. 1 and 4). Full circles: measurements at 300 K, open squares at 20 K, both normalized to a common maximum intensity. All data were corrected for a small tilt of the sample surface against (001). The more pronounced oscillations at E_S are mainly caused by the anti-symmetric dipole-quadrupole term [Eq. (9)]. The solid lines represent calculations according to Eq. (19).

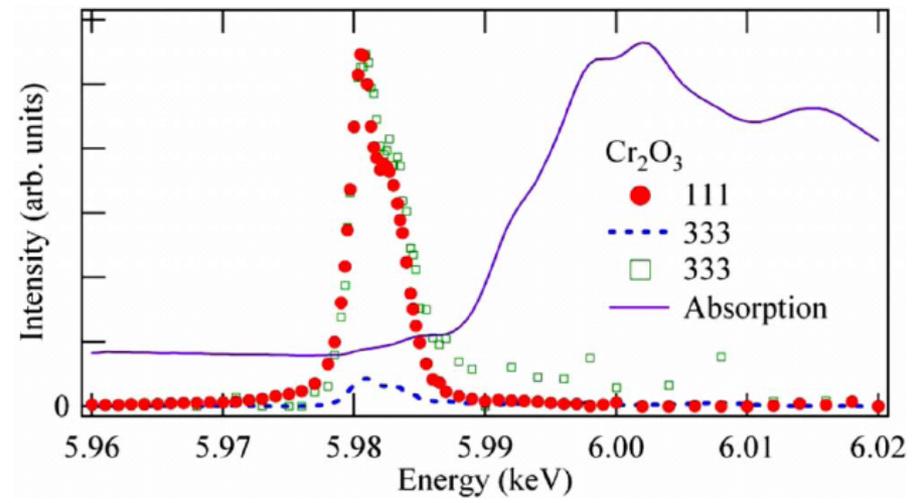
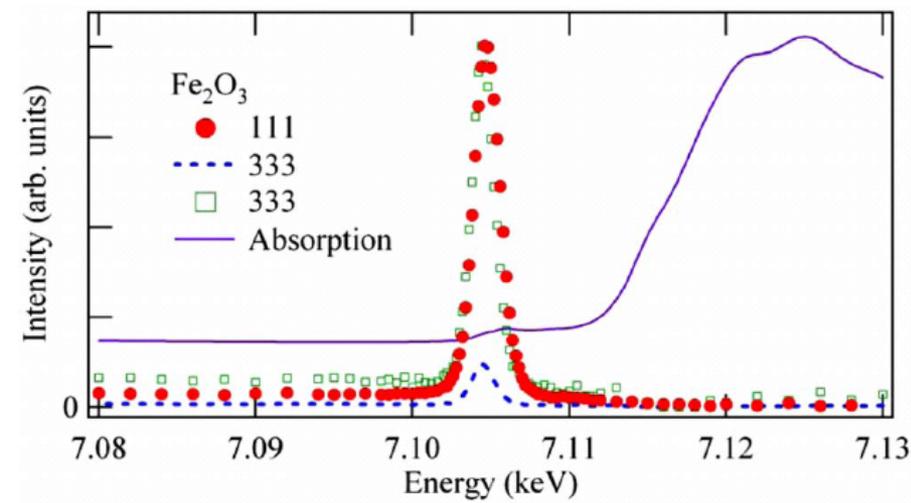
Magnetic and chirality effects in Fe_2O_3 and Cr_2O_3

Small effects in absorption.

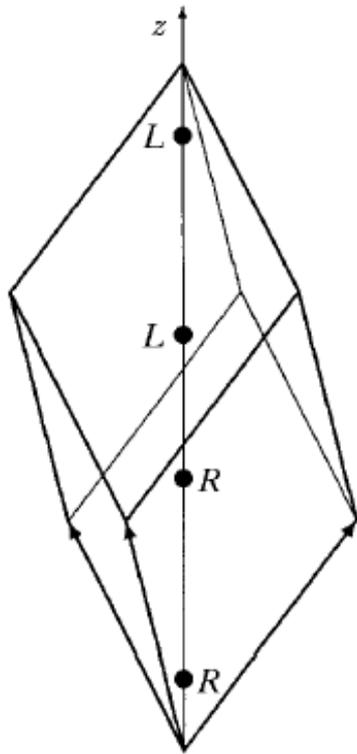
Very rich variety of phenomena in diffraction
owing to interplay of dipole-quadrupole,
quadrupole-quadrupole
and magnetic contributions

CHIRAL AND MAGNETIC EFFECTS IN FORBIDDEN...

PHYSICAL REVIEW B 78, 115112 (2008)



Local chirality of atoms in centrosymmetric crystals



Fe₂O₃, Cr₂O₃;
Kokubun, Ishida, et al.
hhh ATS reflections (h=2n+1)

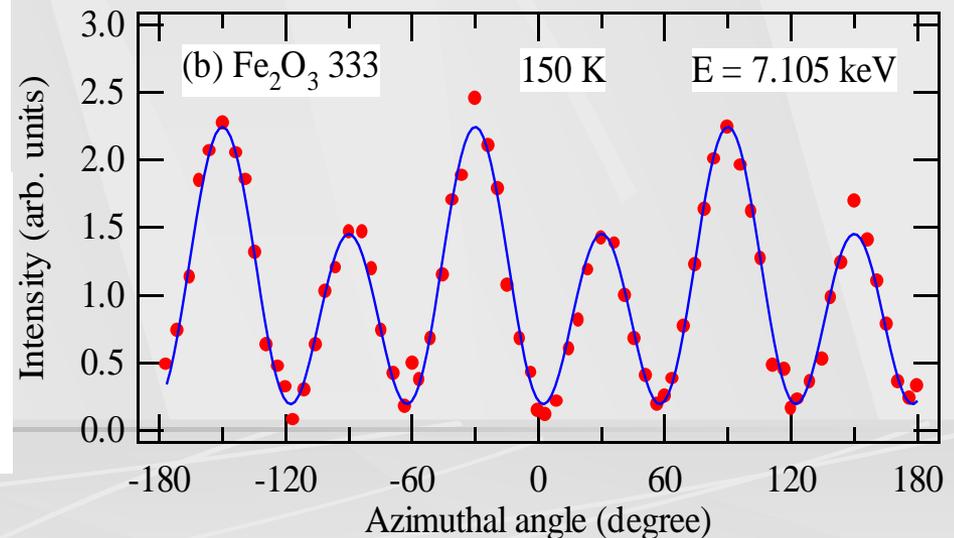
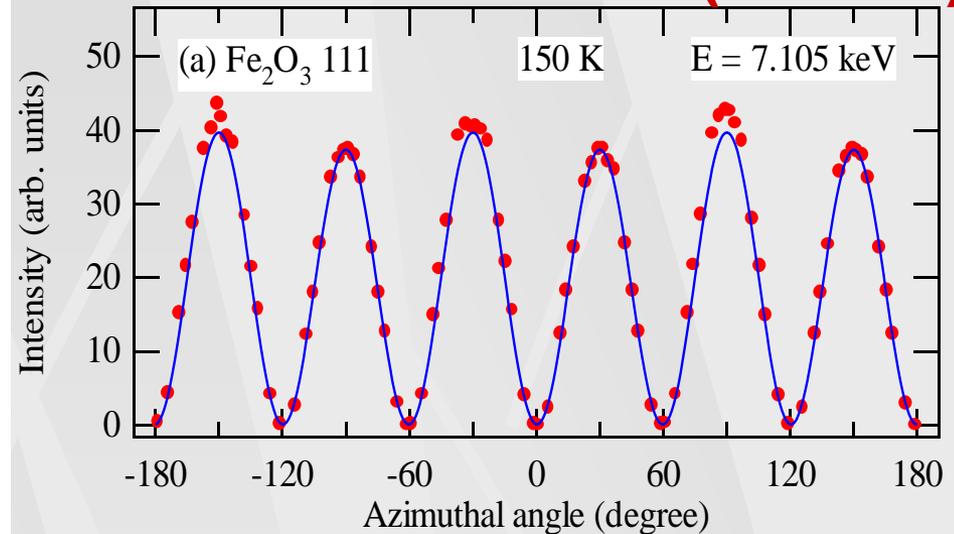


Figure 1
 The 'right-handed' and 'left-handed' positions of Fe atoms in a unit cell of hematite.

$$\begin{aligned} \pi' \hat{\mathbf{F}}(hhh) \sigma &= 8ikf_2^{dqa} \sin(6\pi hx) \cos^2 \theta \\ &\quad + 4 \cos(6\pi hx) f_1^{qq} k^2 \cos^3 \theta \sin 3\varphi, \\ \sigma \hat{\mathbf{F}}(hhh) \pi &= -8ikf_2^{dqa} \sin(6\pi hx) \cos^2 \theta \\ &\quad + 4 \cos(6\pi hx) f_1^{qq} k^2 \cos^3 \theta \sin 3\varphi. \end{aligned}$$

Magnetic structures of Fe₂O₃ and Cr₂O₃

Fe₂O₃:

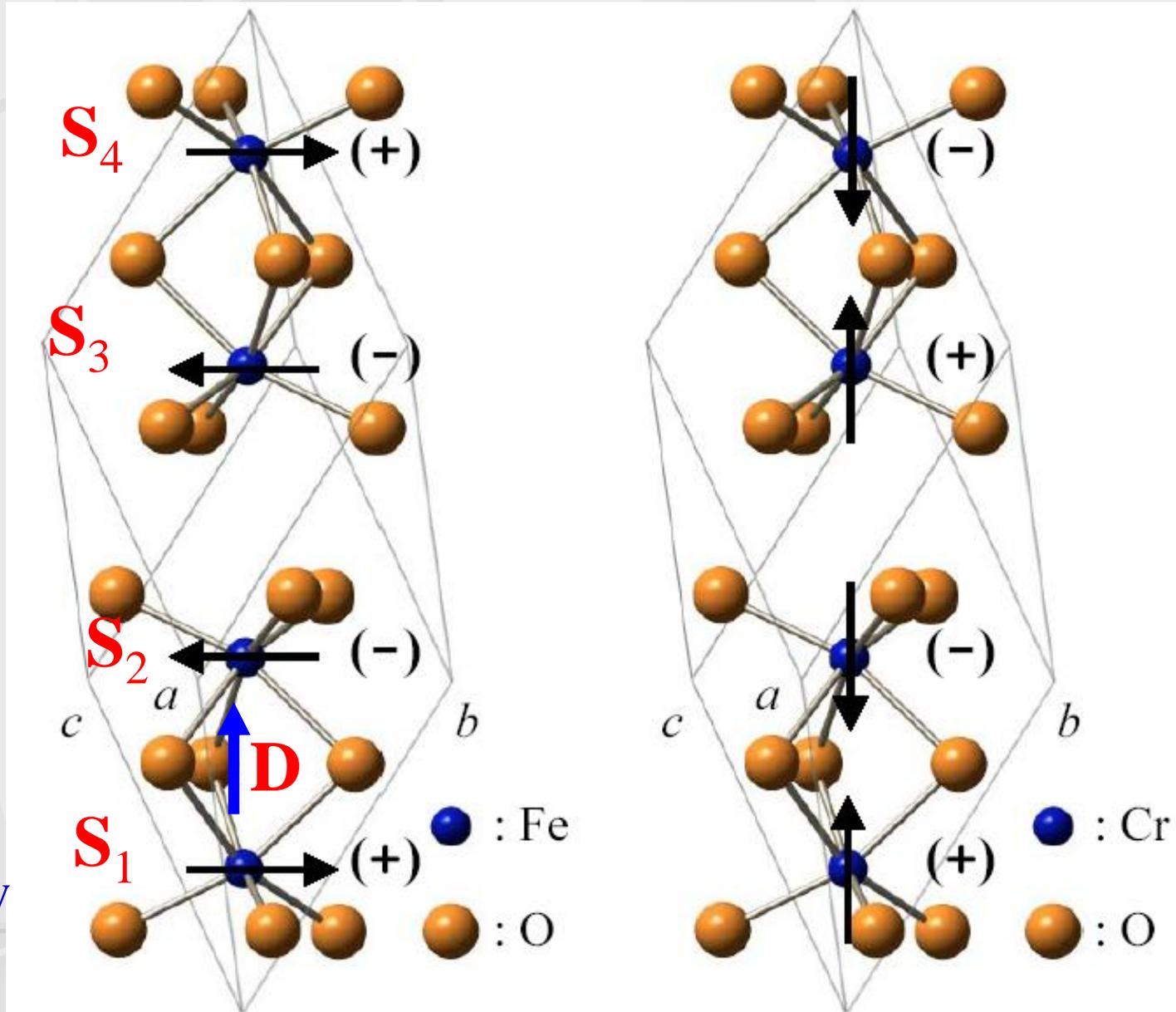
Weak ferromagnetic
due to DM interaction

$$\mathbf{H}_{\text{DM}} = \mathbf{D} \cdot [\mathbf{S}_1 \ \mathbf{S}_2]$$

Owing to this
interaction spins
are canted out of
the figure plane,
the ferromagnetic
moment is normal
to the figure plane.

But in which
direction?

It can be rotated by
a strong enough
magnetic field



Weak ferromagnetism in antiferromagnets: α -Fe₂O₃ and La₂CuO₄V. V. Mazurenko^{1,2} and V. I. Anisimov^{1,2}

theory $\Delta\varphi \approx 0.4 \cdot 10^{-3}$
 experiment $\Delta\varphi \approx 1.1 \times 10^{-3}$

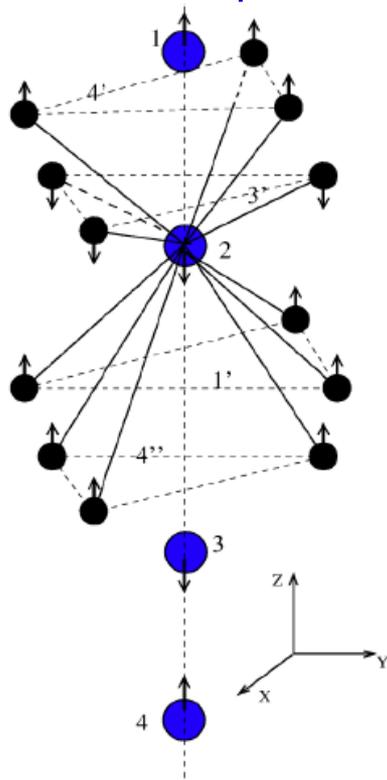
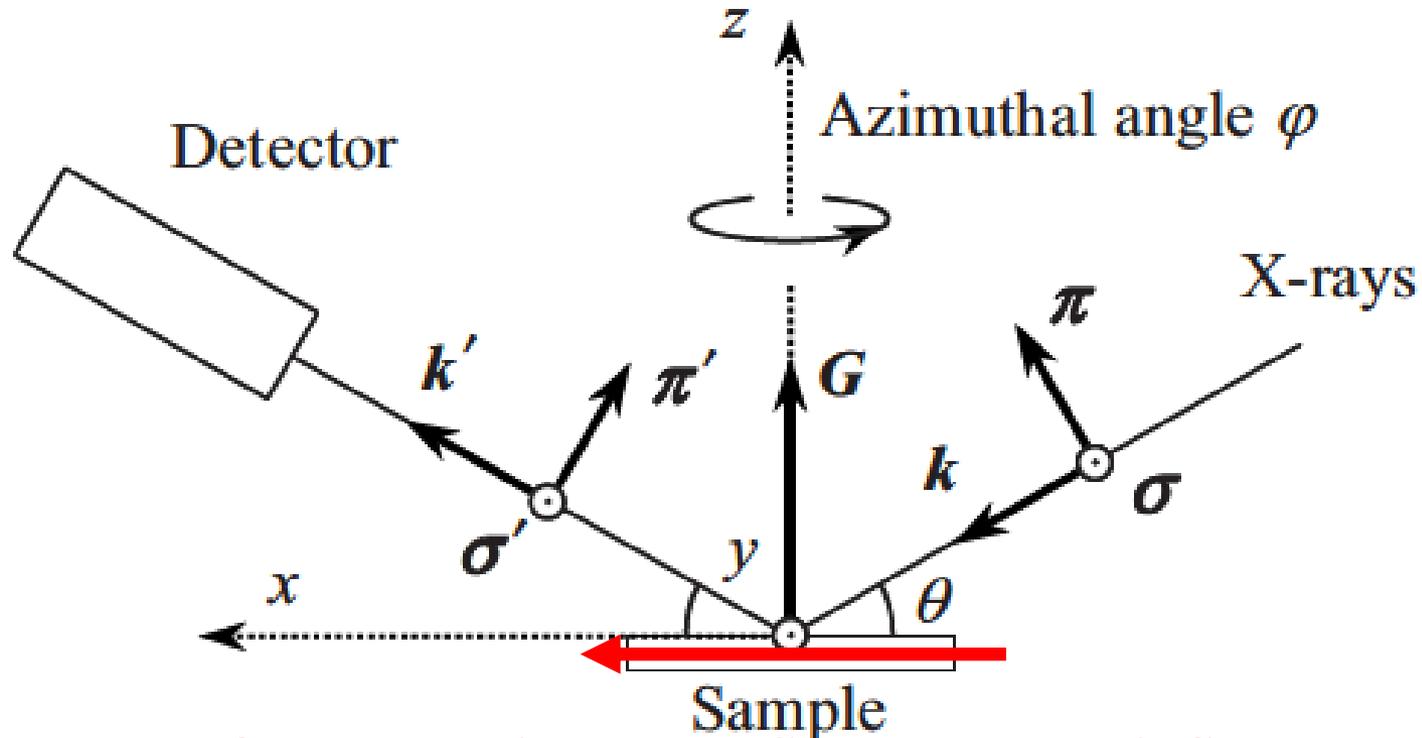


FIG. 1. (Color online) The crystal structure of α -Fe₂O₃. The large circles are Fe atoms which belong to the smallest unit cell used in the LDA+ U calculations. The small circles are Fe atoms which surround atom 2. The arrows denote the magnetic configuration used in our calculations.

TABLE II. The different contributions in components of site magnetic torque of α -Fe₂O₃ obtained in LDA+ U calculation (in meV). The couplings with negative sign are ferromagnetic. d_{ij} is the distance between i th and j th atoms in a.u. \vec{R}_{ij} is the radius vector from i th site to j th site in units of the lattice constant (5.49 a.u.).

(i, j)	d_{ij}	\vec{R}_{ij}	B_{ij}^x	B_{ij}^y	B_{ij}^z
(2,2)	0	(0;0;0)	0	0	0.162
(2,1)	5.45	(0;0;-0.99)	0	0	0.005
(2,3')	5.60	(-0.5;-0.86;0.20)	-0.036	0.015	0.001
(2,3')	5.60	(1;0;0.20)	0.032	0.023	0.001
(2,3')	5.60	(-0.5;0.86;0.20)	0.004	-0.038	0.001
(2,1')	6.36	(0.5;-0.86;-0.58)	0.071	0.019	-0.14
(2,1')	6.36	(-1;0;-0.58)	-0.052	0.052	-0.14
(2,1')	6.36	(0.5;0.86;-0.58)	-0.019	-0.071	-0.14
(2,4')	6.99	(0.5;-0.86;0.79)	0.168	0.063	0.101
(2,4')	6.99	(-1;0;0.79)	-0.139	0.115	0.101
(2,4')	6.99	(0.5;0.86;0.79)	-0.029	-0.178	0.101
(2,4'')	6.99	(-0.5;-0.86;-0.79)	0.128	0.094	0.076
(2,4'')	6.99	(1;0;-0.79)	0.017	-0.158	0.076
(2,4'')	6.99	(-0.5;0.86;-0.79)	-0.145	0.064	0.076
(2,4)	7.53	(0;0;-1.37)	0	0	0.001

Typical setup



h - weak ferromagnetic moment fixed by magnetic field

FIG. 2. Definition of the optical setting. σ and π denote polarization vectors for the incident x rays, σ' and π' for the scattering x rays. k and k' denote the wave vectors for the incident and scattering x rays, respectively, G the scattering vector; z axis is parallel to the threefold crystal axis, and the x axis is normal to one of three vertical glide planes and parallel to the hexagonal a axis. When the azimuthal angle φ equals zero, vector $k+k'$ coincides with the x axis; just this case is shown in the figure. X-ray beam is rotated clockwise viewed from $+z$ side with the angle φ , i.e., sample crystal is rotated counterclockwise relative to the x-ray beam.

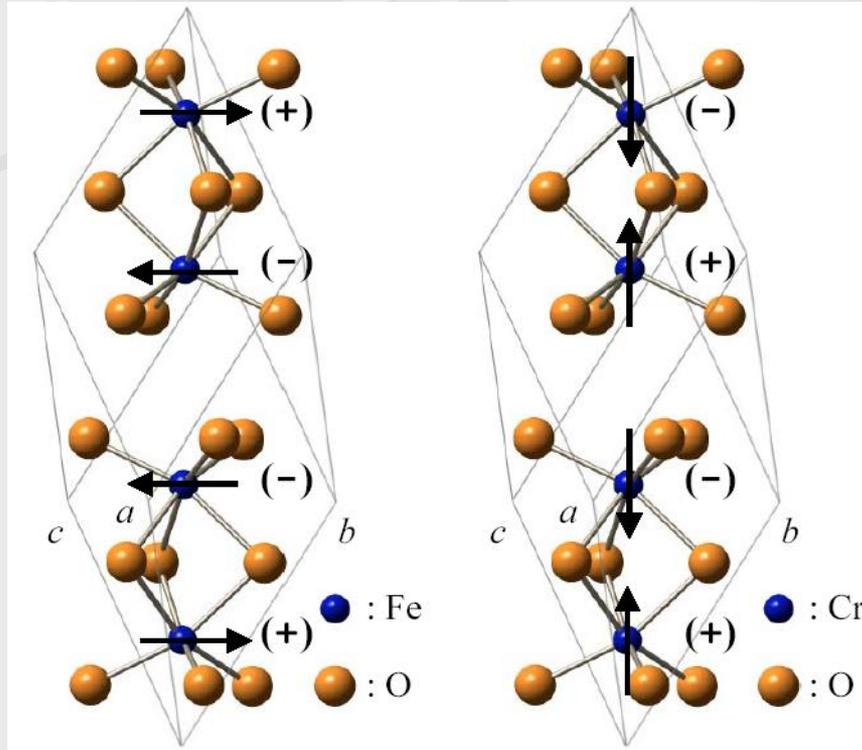
Magnetic structures of Fe_2O_3 and Cr_2O_3

Fe_2O_3 :

1) Interference of non-resonant magnetic term and resonant d-q and q-q terms.

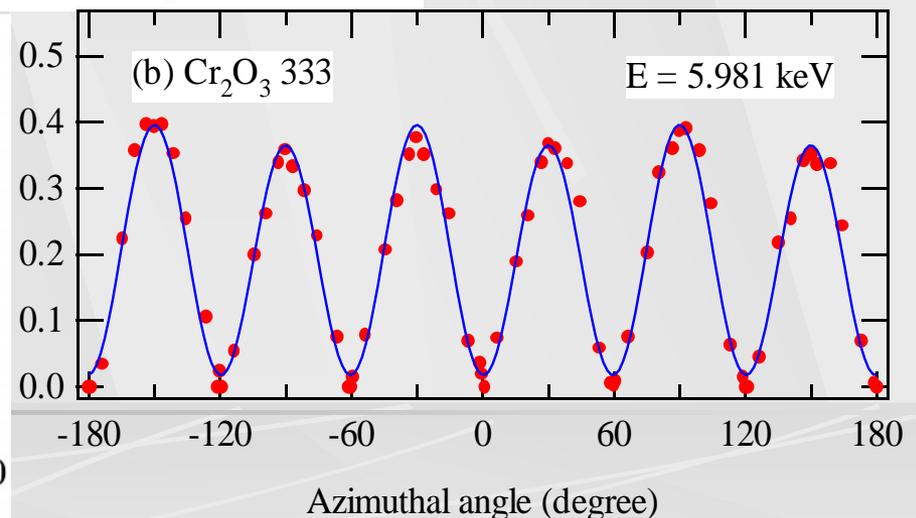
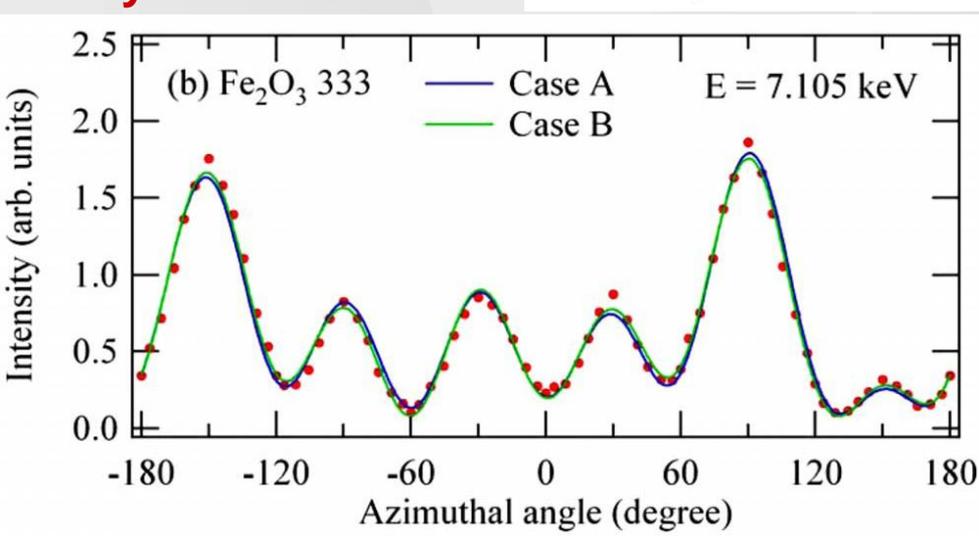
2) Single-domain antiferromagnetic structure

1) and 2) allow us to measure the sign of the Dzyaloshinskii-Moriya interaction!



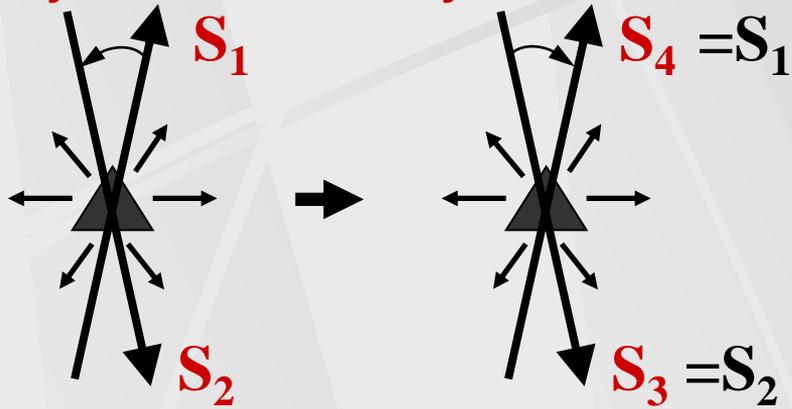
Cr_2O_3 :

Interference of resonant d-q and q-q terms but no magnetic contribution to diffraction

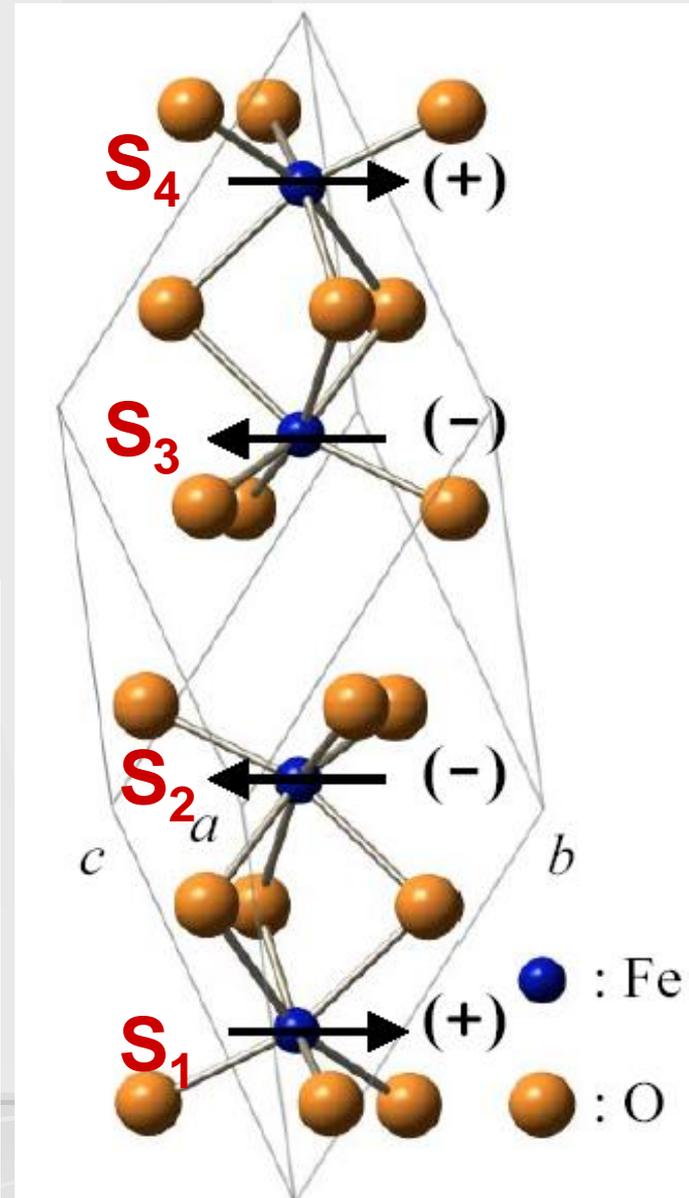
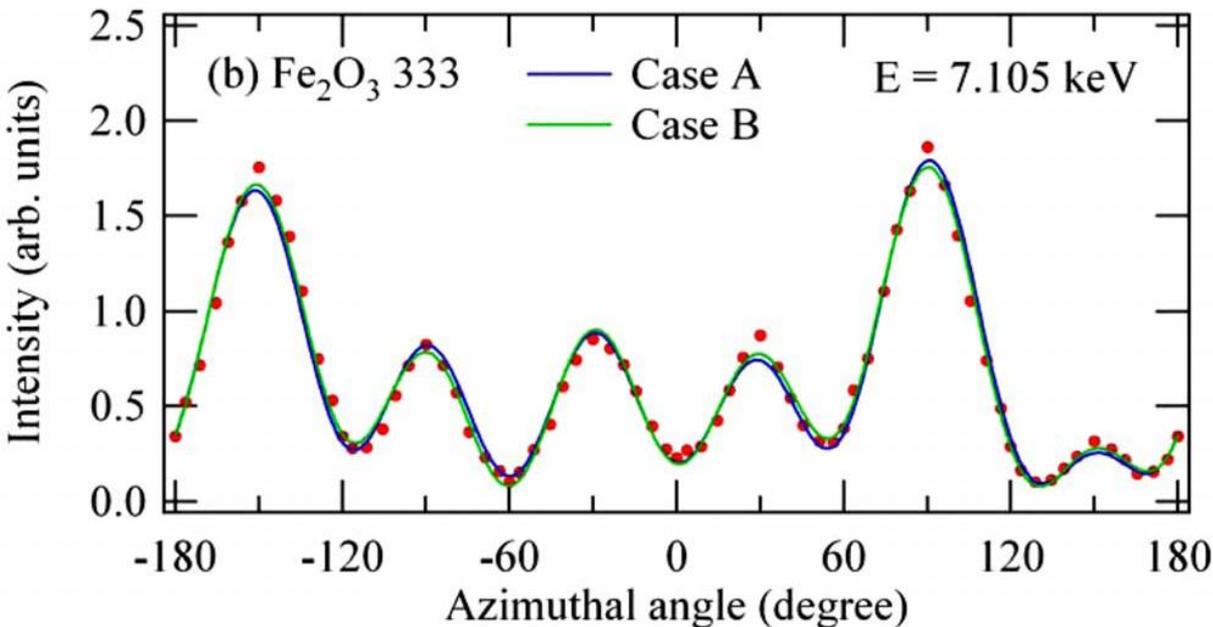


Sign of the Dzyaloshinskii-Moriya interaction

Fe_2O_3 – weak ferromagnetic owing to the Dzyaloshinskii-Moriya interaction $\mathbf{D} \cdot [\mathbf{S}_1 \times \mathbf{S}_2]$

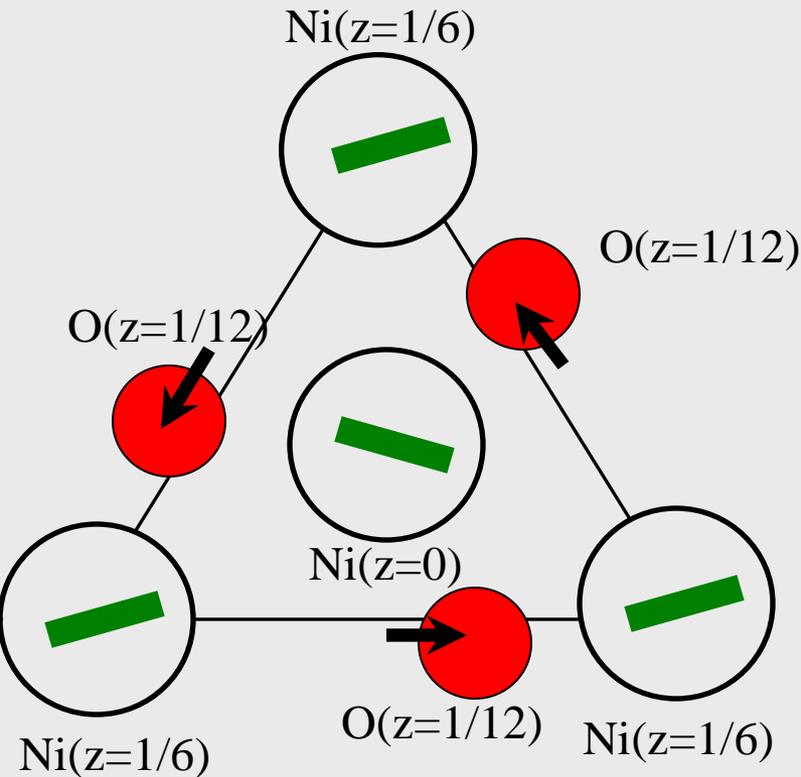


right-hand twist left-hand twist



Локальная хиральность как причина слабого ферромагнетизма в структуре типа NiCO_3 ($R\bar{3}c$)

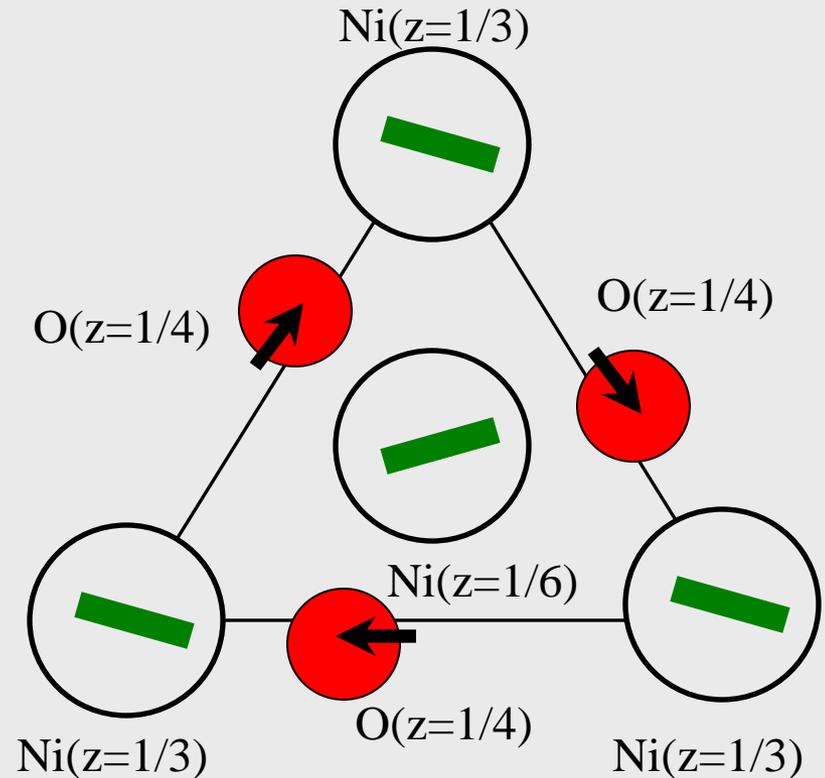
от $z=0$ к $z=1/6$: **правая** подкрутка кислородного треугольника



от $z=0$ к $z=1/6$: пусть тоже **правая** подкрутка магнитного момента

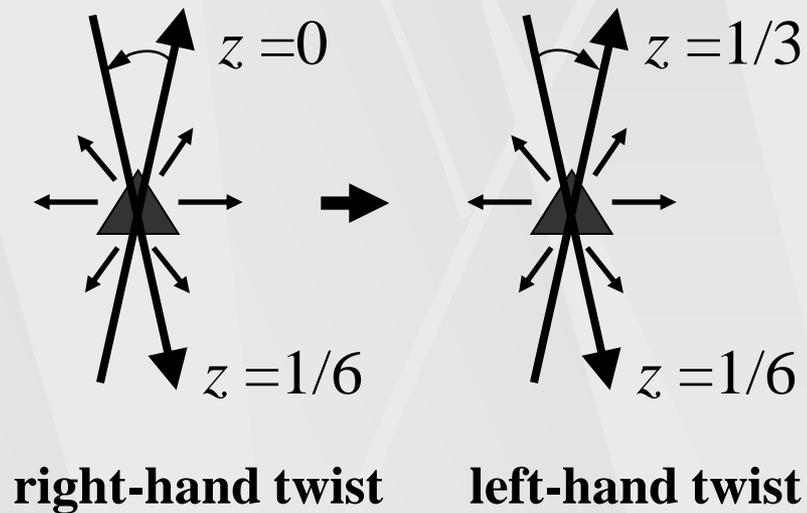
Атомы Ni взаимодействуют через «хиральные» атомы кислорода

от $z=1/6$ к $z=1/3$: **левая** подкрутка кислородного треугольника



от $z=1/6$ к $z=1/3$: соответственно **левая** подкрутка магнитного момента

Local twist of moments from layer to layer in MnCO_3



Neutron diffraction for sign measurements

Interference
between magnetic
scattering and
nuclear scattering
on oxygen atoms.
Oblique reflections
 hkl should be used:
 $l=2n+1, hk(h+k)\neq 0$.

The sign can be
deduced from
 $R(hkl) > 1$ or $R(hkl) < 1$

In the case of neutron diffraction, one can adopt the standard technique using the polarization ratio R , i.e. the ratio of reflection intensities for incoming neutrons with spin σ parallel and antiparallel to the direction of applied magnetic field. For $l = 2n + 1$ this ratio is given by the following expression containing interference between nuclear scattering by oxygen atoms and magnetic scattering by Mn atoms

$$R(hkl) = \frac{|F_{ox}(\mathbf{H}) + \sigma \cdot \mathbf{Q}(\mathbf{H})|^2}{|F_{ox}(\mathbf{H}) - \sigma \cdot \mathbf{Q}(\mathbf{H})|^2} \quad (5)$$

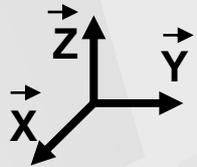
$$= \frac{|F_{ox}(\mathbf{H}) - s_{DM} A_{mag} k(2h + k)|^2}{|F_{ox}(\mathbf{H}) + s_{DM} A_{mag} k(2h + k)|^2}, \quad (6)$$

where $\mathbf{Q}(\mathbf{H})$ is the magnetic structure amplitude for reflection \mathbf{H} , $\mathbf{Q}(\mathbf{H}) \propto \mathbf{M}_{\mathbf{H}} - \mathbf{H}(\mathbf{H} \cdot \mathbf{M}_{\mathbf{H}})/H^2$, $\mathbf{M}_{\mathbf{H}}$ is the correspondent Fourier harmonic of the vector field describing the electron-magnetization distribution, s_{DM} is the sign of the Dzyaloshinskii–Moriya interaction between the first two layers of Mn atoms and A_{mag}

Conclusions

- The sign of the Dzyaloshinskii-Moriya interaction can be measured in single crystals of weak ferromagnetics using resonant X-ray diffraction, neutron diffraction, or Mössbauer diffraction.
- The crucial features are 1) interference between magnetic and structural channels of scattering and 2) a single-domain magnetic state.

Phase B₂ – proposed structures (Link et al. 1997)



Glide plane YZ

Glide plane XZ

Screw axis 2₁ Z

Réflexion + translation

Réflexion + translation

Rotation 180° + translation

~~Ferro
Synclinique~~

~~SmC_SP_F~~

Ferro
Anticlinique

SmC_AP_F

AntiFerro
Synclinique

SmC_SP_A

AntiFerro
Anticlinique

SmC_AP_A

Однослойная

Cady et al, Liquid Crystals, 2002

Двухслойные

запрещенные
рефлексы



Polarization Studies of Resonant Forbidden Reflections in Liquid Crystals

P. Fernandes,¹ P. Barois,¹ S. T. Wang,² Z. Q. Liu,² B. K. McCoy,² C. C. Huang,² R. Pindak,³ W. Caliebe,³ and H. T. Nguyen¹

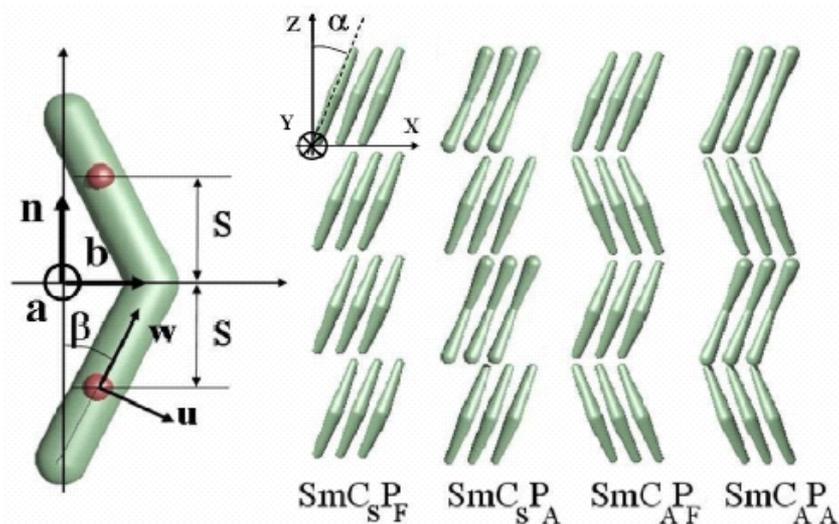


FIG. 1 (color online). (a) Left: Schematic view of a bent-core molecule as a bow. The orientation of the string and arrow are described by unit vectors \mathbf{n} and \mathbf{b} , respectively. (b) Right: Sketch of four possible arrangements in the B_2 phase. α is the SmC-like tilt of the string over the layer normal. The structures $\text{SmC}_S P_F$ and $\text{SmC}_A P_A$ are chiral, whereas $\text{SmC}_S P_A$ and $\text{SmC}_A P_F$ are racemic mixtures of chiral layers.

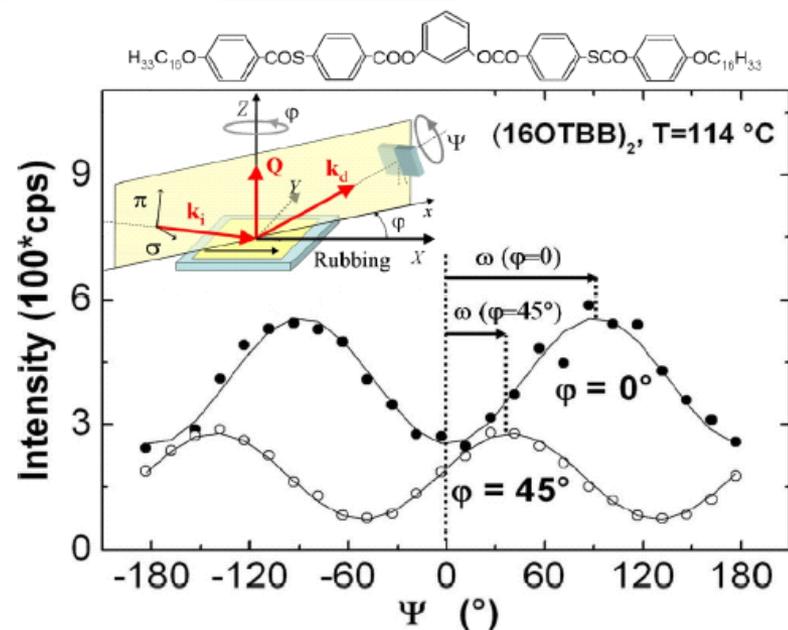


FIG. 2 (color online). ψ scans of the polarization analyzer for the $3/2$ resonant peak. The intensity maxima, labeled by the angle ω , indicate the rotation in polarization of the diffracted beam relative to the σ polarized incident beam. φ is the angle between the sample rubbing direction and the scattering plane (see inset). The molecule $(16\text{OTBB})_2$ is shown on top.

Показали, что из четырех фаз наиболее вероятна одна, $\text{SmC}_S P_A$

Exploiting the anisotropy of anomalous scattering boosts the phasing power of SAD and MAD experiments

Marc Schiltz^{a,b*} and Gérard Bricogne^b

The X-ray polarization anisotropy of anomalous scattering in crystals of brominated nucleic acids and selenated proteins is shown to have significant effects on the diffraction data

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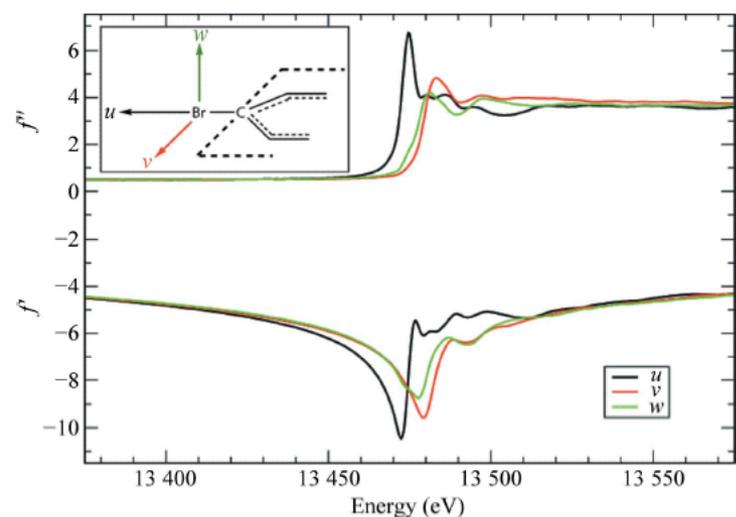


Figure 2

Anomalous scattering factors f' and f'' for Br in brominated nucleotides. The curves represent the anomalous scattering factors when the polarization direction of the incident X-ray beam is aligned with one of the principal molecular directions in a brominated nucleobase. Black curves: along the direction u (parallel to the C–Br bond). Red curves: along the direction v (perpendicular to the C–Br bond and parallel to the plane of the nucleobase ring). Green curves: along the direction w (perpendicular to the nucleobase ring). Data from Sanishvili *et al.* (2007).

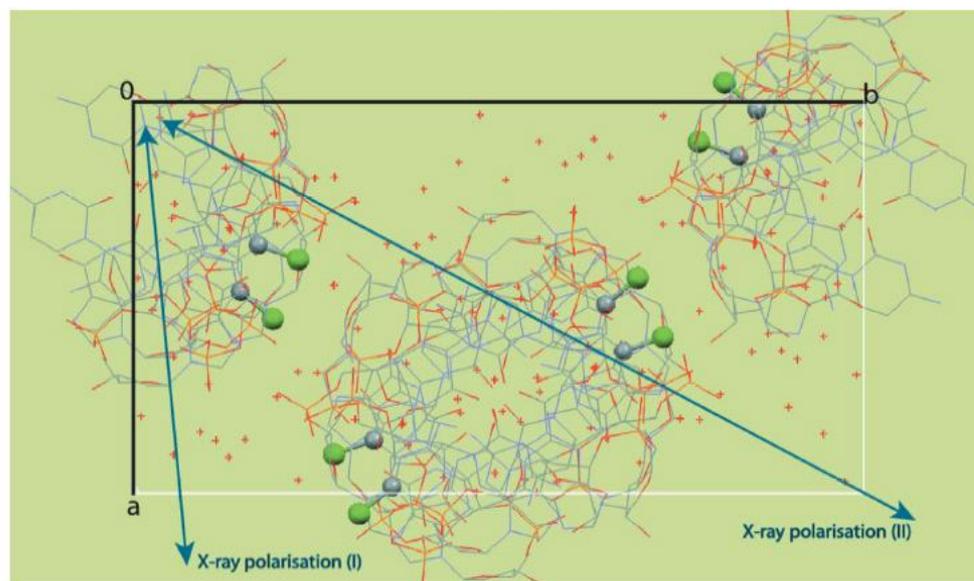


Figure 4

Packing of $d(CGCG[BrU]G)$ molecules viewed down the crystal c axis. The eight C–Br moieties in the unit cell are displayed, with the Br atoms highlighted as green spheres. Owing to the orientation of the helical DNA duplexes in the crystal, all C–Br bonds are oriented almost perpendicular to $[001]$. Also displayed is the in-plane component of the X-ray polarization direction for data sets (I) and (II). {For data set (III), the X-ray polarization direction was almost parallel to $[001]$ and is therefore not displayed here.}

Использование рентгеновской анизотропии в структурном анализе

Table 1

Data-collection and processing statistics for the brominated Z-DNA duplex d(CGCG[BrU]G).

Values in parentheses are for the outer resolution shell.

	Data set (I)	Data set (II)	Data set (III)
X-ray polarization direction† (p)	$\begin{pmatrix} 0.989 \\ 0.112 \\ -0.095 \end{pmatrix}$	$\begin{pmatrix} 0.427 \\ 0.767 \\ -0.480 \end{pmatrix}$	$\begin{pmatrix} 0.162 \\ -0.123 \\ -0.979 \end{pmatrix}$
X-ray wavelength (Å)/photon energy (keV)	0.9199/13.477		
Rotation per image (°)	1	1	1
Exposure time per image (s)	2.2	2.2	2.2
Total No. of images	145	145	149
Space group	$P2_12_12_1$		
Unit-cell parameters (Å, °)	$a = 17.34, b = 32.07, c = 44.34, \alpha = \beta = \gamma = 90$		
Resolution limits (Å)	32.1–1.10 (1.16–1.10)	30.0–1.10 (1.16–1.10)	32.1–1.10 (1.16–1.10)
No. of measured reflections	41485 (1004)	41428 (1001)	42675 (1041)
No. of unique reflections in Laue group mmm	8303 (443)	9306 (603)	8542 (497)
No. of unique reflections in Laue group $\bar{1}$	26133 (695)	26151 (694)	26371 (700)
R_{meas} in point group $222\ddagger$	0.073 (0.292)	0.090 (0.289)	0.059 (0.174)
$R_{\text{meas}0}$ in Laue group $mmm\§$	0.096 (0.302)	0.130 (0.321)	0.066 (0.252)
R_{meas} in point group $\bar{1}$	0.090 (0.288)	0.104 (0.401)	0.074 (0.253)
$R_{\text{meas}0}$ in Laue group $\bar{1}$	0.108 (0.305)	0.153 (0.328)	0.071 (0.257)

† All vectors are expressed on a crystal Cartesian basis ($\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$) which sets \mathbf{e}_x parallel to \mathbf{a} and \mathbf{e}_z parallel to \mathbf{c}^* . ‡ Multiplicity-weighted merging R factor, keeping Bijvoet pairs separate (*i.e.* computed in the crystal point group). § Multiplicity-weighted merging R factor, not keeping Bijvoet pairs separate (*i.e.* computed in the crystal Laue group).

ЗАКЛЮЧЕНИЕ КАМО ГРЯДЕШИ? (QUO VADIS?)

Рентгеновская спектроскопия и резонансная дифракция позволяют изучать искажения электронных состояний атомов в кристаллах. Эти методы **селективны** по краю поглощения.

Поляризационные измерения (линейный и круговой дихроизм, поляризационные свойства дифракции) дают информацию об анизотропии таких искажений.

Резонансная дифракция и, особенно, «запрещённые» рефлексы позволяют полностью определить анизотропию восприимчивости, в частности, различать свойства атомов одного элемента, находящихся в разных положениях.

Анизотропия может индуцироваться тепловыми колебаниями. В **центросимметричных** кристаллах можно измерить локальную «**хиральность**» атомов с правым и левым окружением.

Заключение (продолжение)

В магнитных структурах можно определять весьма тонкие особенности: разделять спиновый и орбитальный вклад в кристаллах и пленках;

измерять знак взаимодействия Дзялошинского-Мория.

Современные программы расчётов дают возможность **количественного** описания рентгеновских спектров и резонансной дифракции.

Особенно интересным является использование рентгеновской анизотропии в **биологических** системах, так как в них тяжёлые атомы обычно имеют важные биологические функции и электронные состояния атомов могут меняться в процессе этих функций.

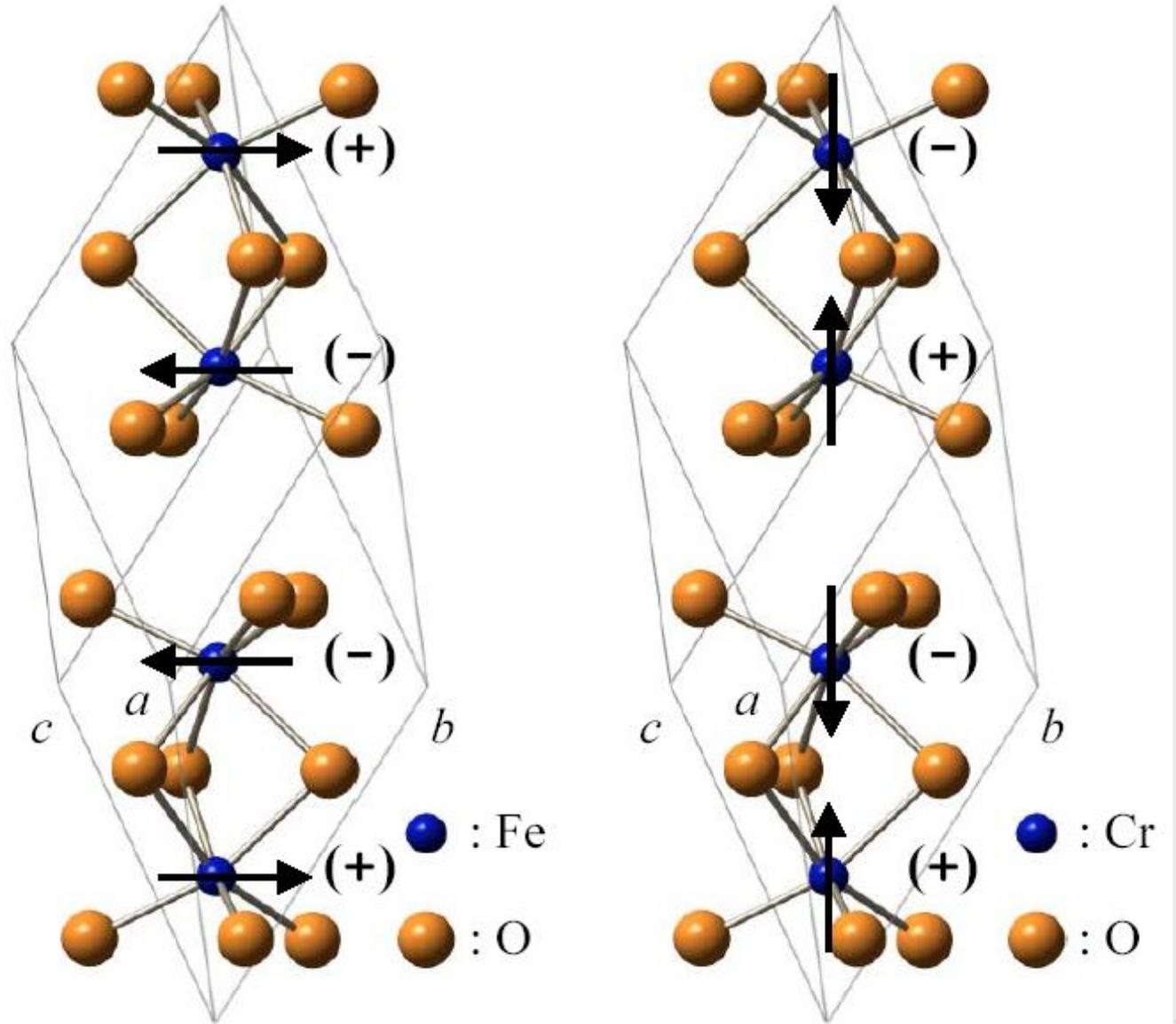
Благодарность нашим соавторам за многолетнее сотрудничество:

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Спасибо за внимание!

Magnetic structure of Fe_2O_3 and Cr_2O_3

Fe_2O_3 : Interference of non-resonant magnetic term and resonant d-q term. Single-domain antiferromagnetic structure



Определение параметров из азимутальных зависимостей для Fe_2O_3

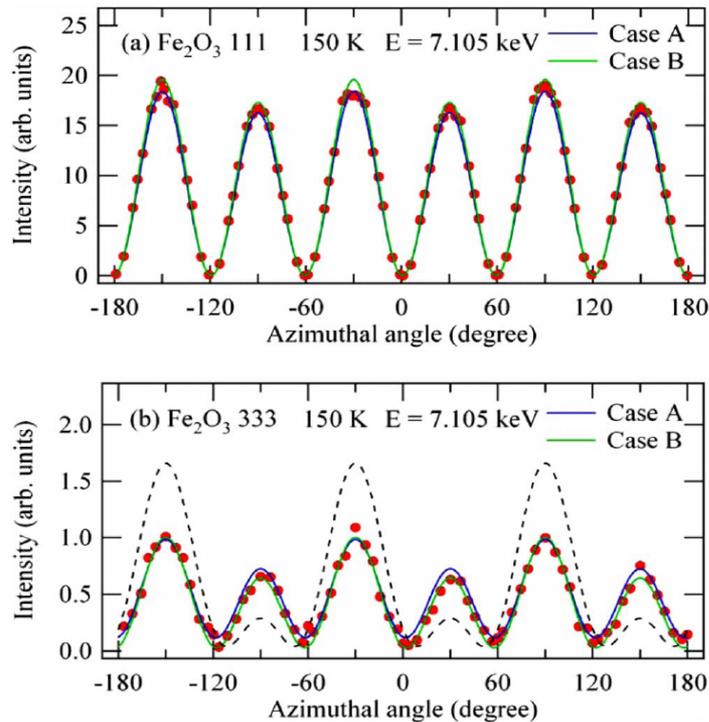


FIG. 10. (Color online) The azimuthal angle dependence of the hematite reflections at 150 K at the resonant energy, 7.105 keV: (a) 111 and (b) 333. The solid curves are calculated by Eq. (22) based on the results of fitting for the 333 reflection at room temperature [see Fig. 11(b) and columns “Case A” and “Case B” in Table I], where we should note that the spin direction is changed by 90 degrees. The dashed curve in (b) represents similar calculation but the spin direction is reversed compared to the condition of the solid curve in Case B.

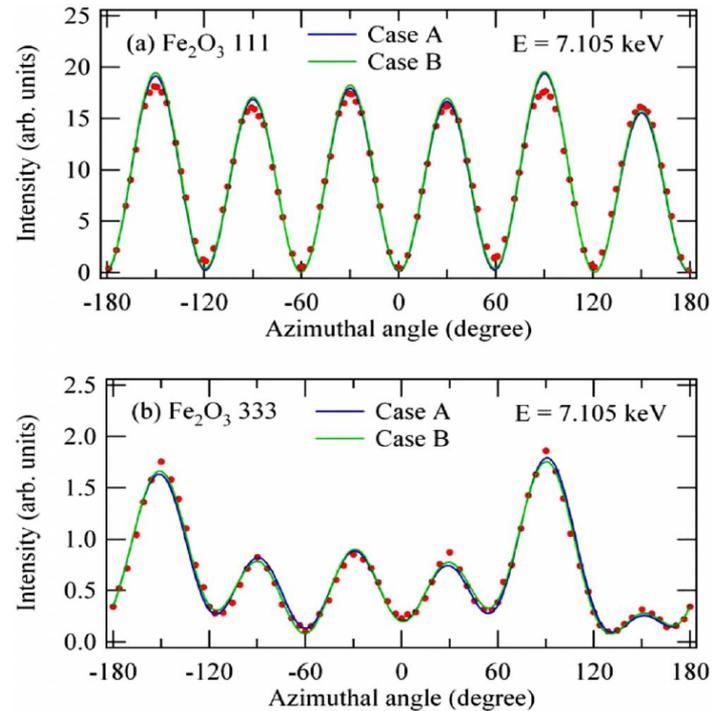


FIG. 11. (Color online) The azimuthal angle dependence of hematite at the room temperature: all experimental results (closed circle) are the same as in Fig. 5. The solid curves in (b) are results of fitting for the 333 reflection by Eq. (22) and the solid curves in (a) are calculated from these results (see “Case A” and “Case B” in Table I).

$$\begin{aligned}
 I_{hh} = & 16|s|^2 \sin^2(\varphi + \beta) \sin^2(2\theta) \cos^2(6\pi hx) \\
 & + |8q_2 \cos^2 \theta \sin(6\pi hx) \\
 & + 4p_7 \sin 3\varphi \cos^3 \theta \cos(6\pi hx) - 8i\{s \cos(\varphi + \beta) \\
 & \times \sin^2 \theta \cos \theta - s_z \sin^3 \theta\} \cos(6\pi hx)|^2, \quad (22)
 \end{aligned}$$