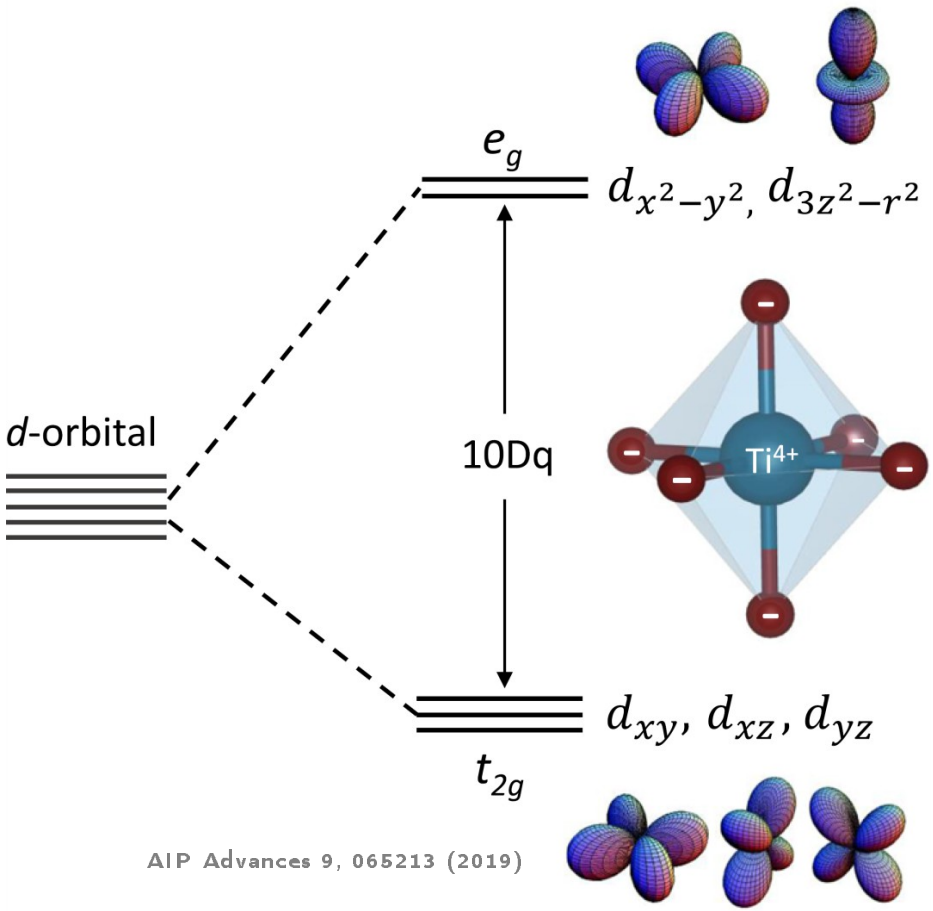
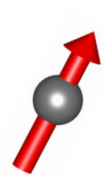
Crystal-field theory



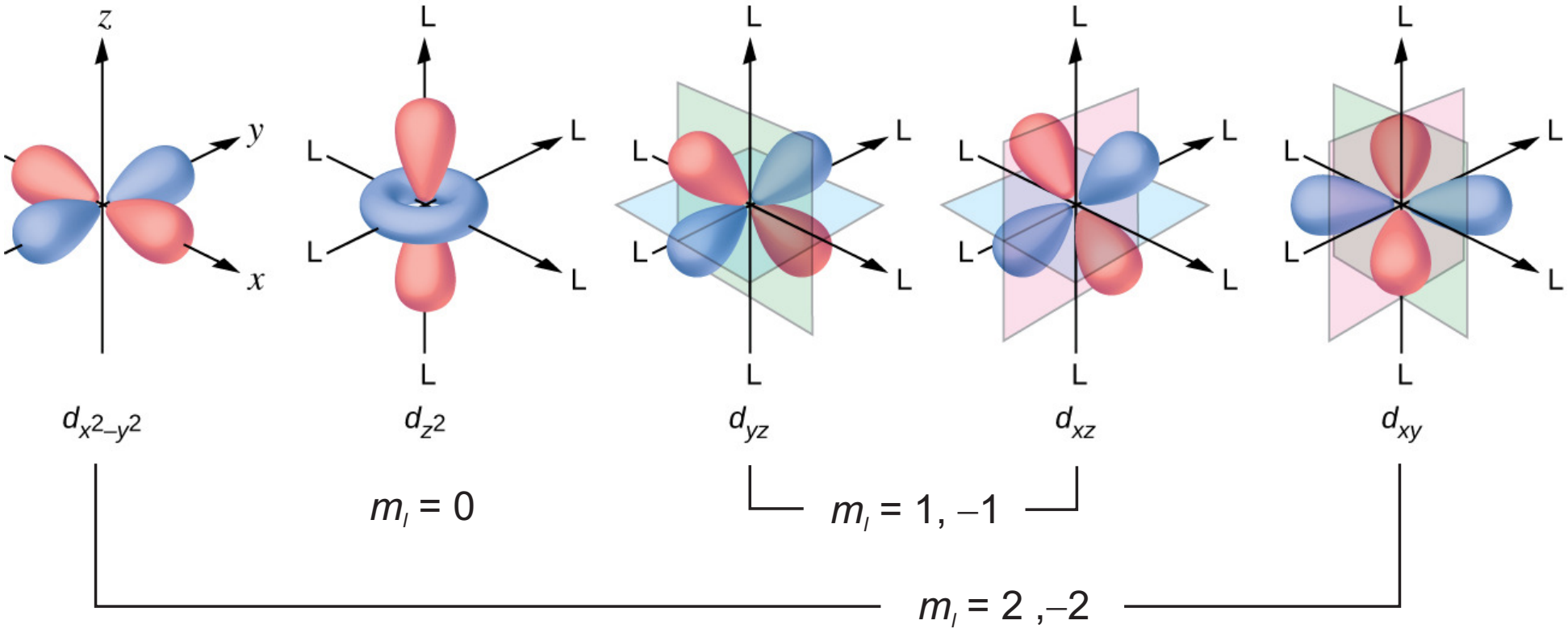
AIP Advances 9, 065213 (2019)



by Alexander Tsirlin, Leipzig University

Tutorial 4: November 12, 2024

Shapes of *d*-orbitals



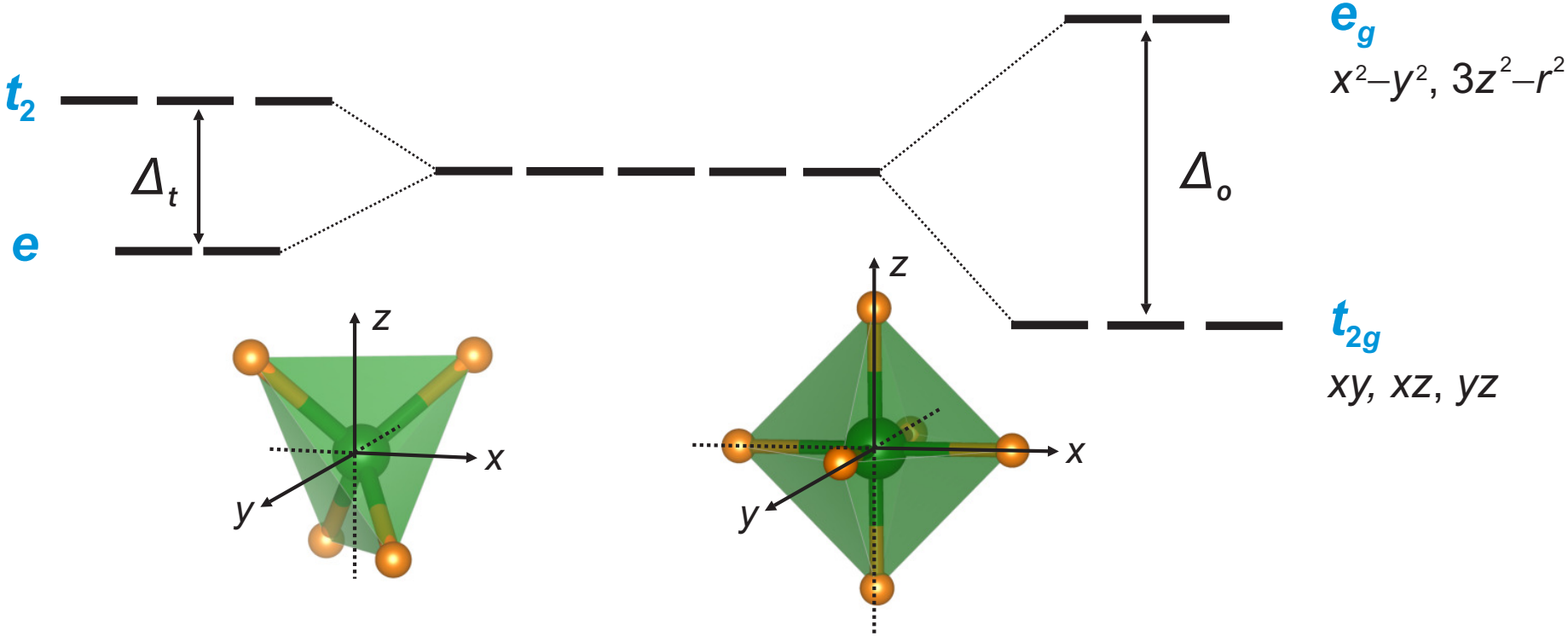
Spherical harmonics, $Y_m^l(\theta, \varphi)$, or their combinations:

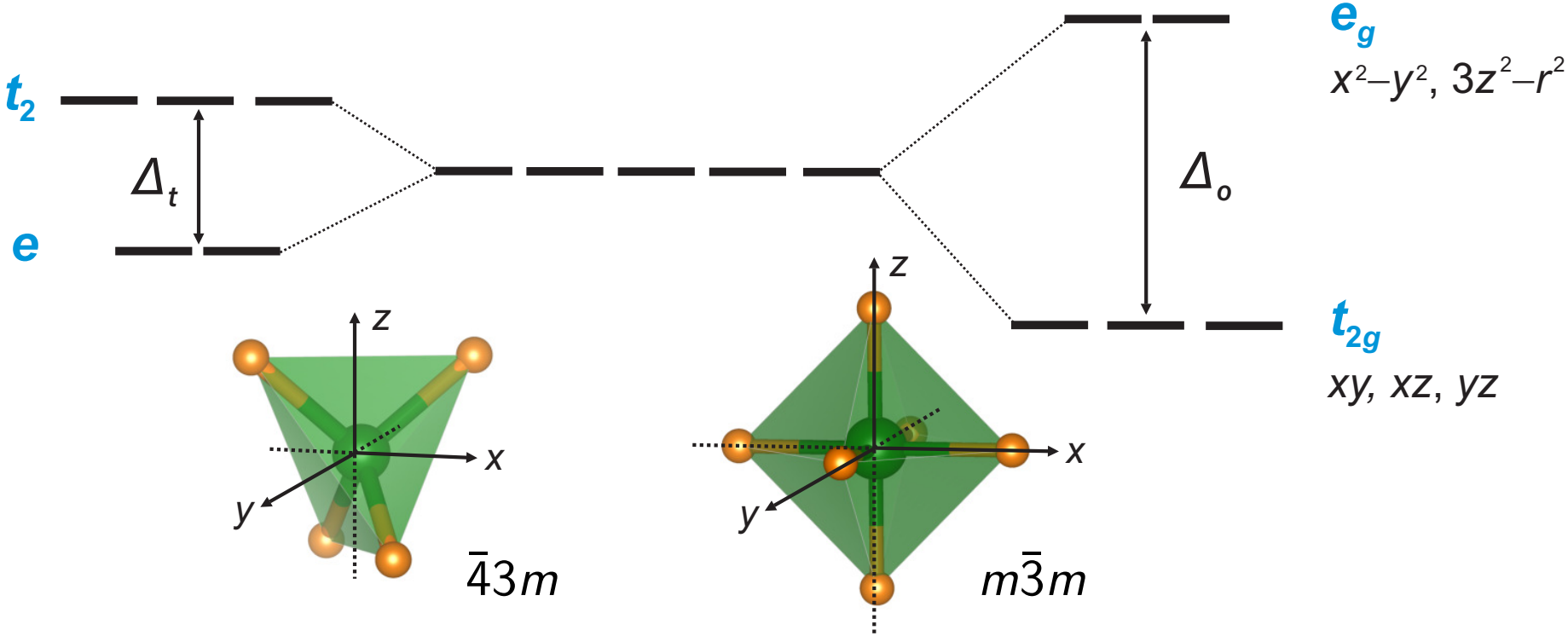
$|3z^2 - r^2\rangle = Y_0^2$

$|x^2 - y^2\rangle = \frac{1}{\sqrt{2}}(Y_2^2 + Y_{-2}^2)$

...

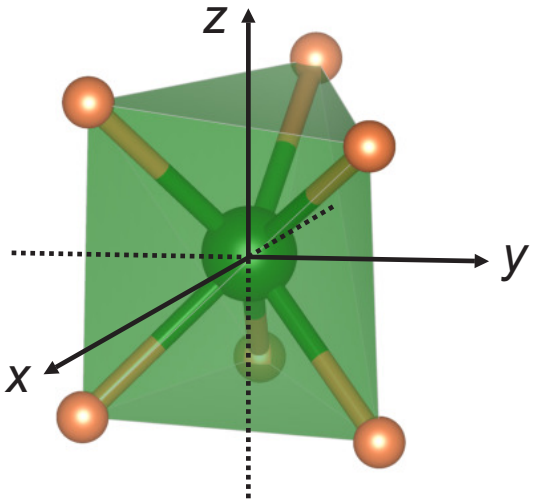
Crystal-field splitting

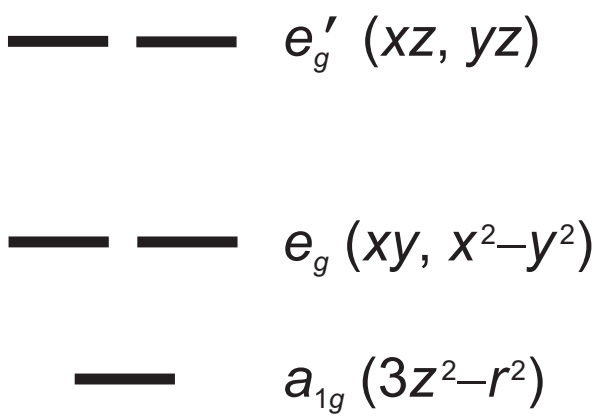




Crystal-field levels are labeled by

irreducible representations of the symmetry group



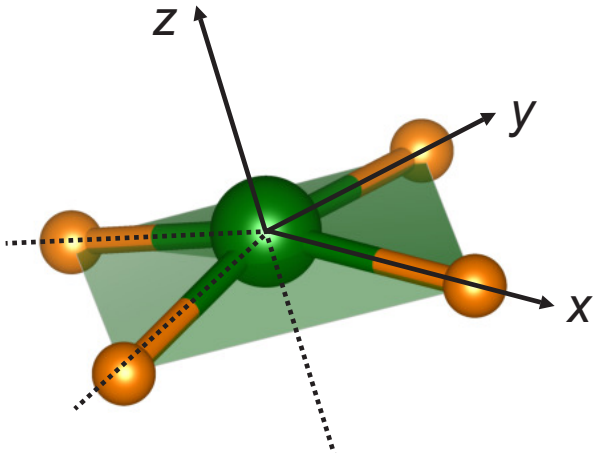


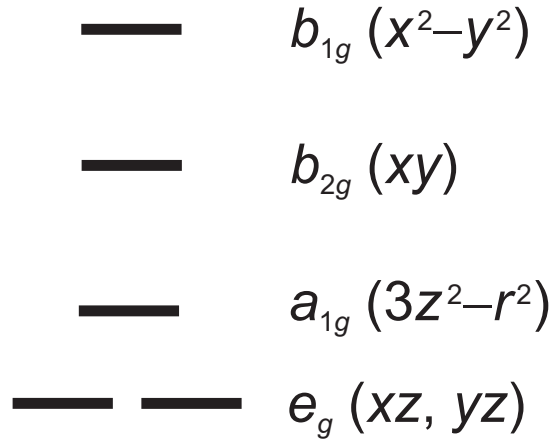
Trigonal prism

symmetry group
D_{3h} $(\bar{6}m2)$

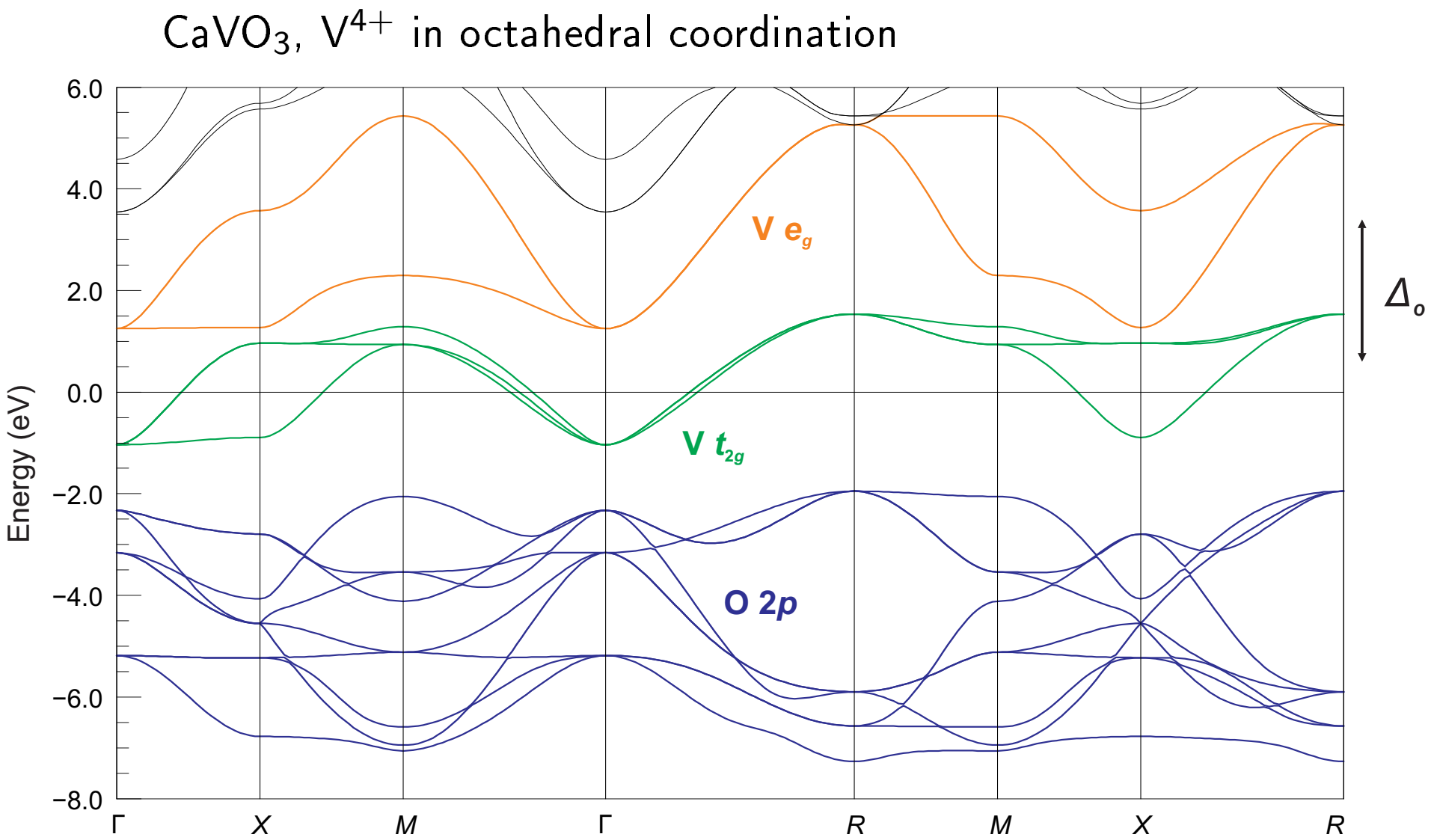
Square plane

symmetry group
D_{4h} $(4/mmm)$





Crystal-field splitting in a band structure



Colors of chromium

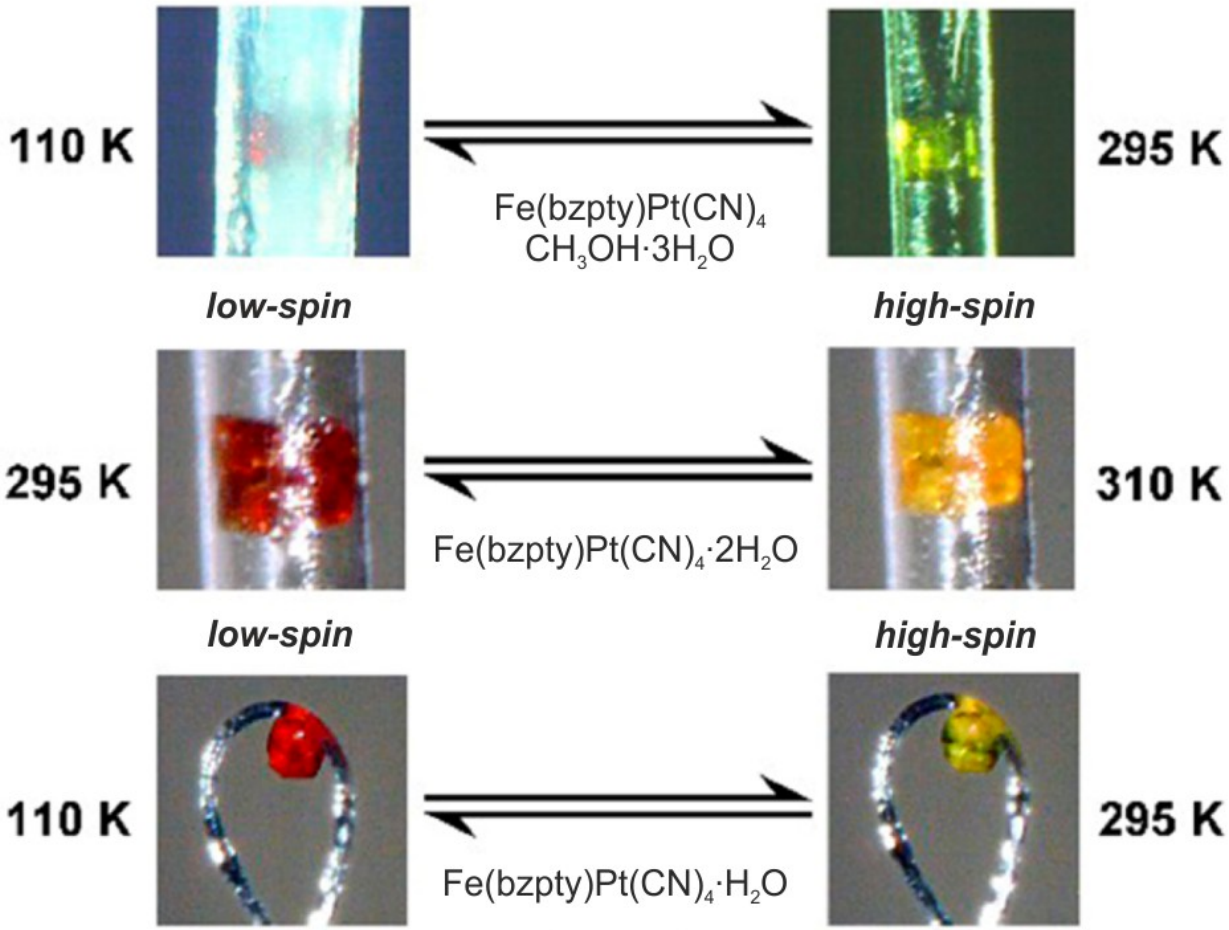
Ruby

Cr^{3+} in corundum, Al_2O_3

Emerald

Cr^{3+} in beryl, $Be_3Al_2Si_6O_{18}$

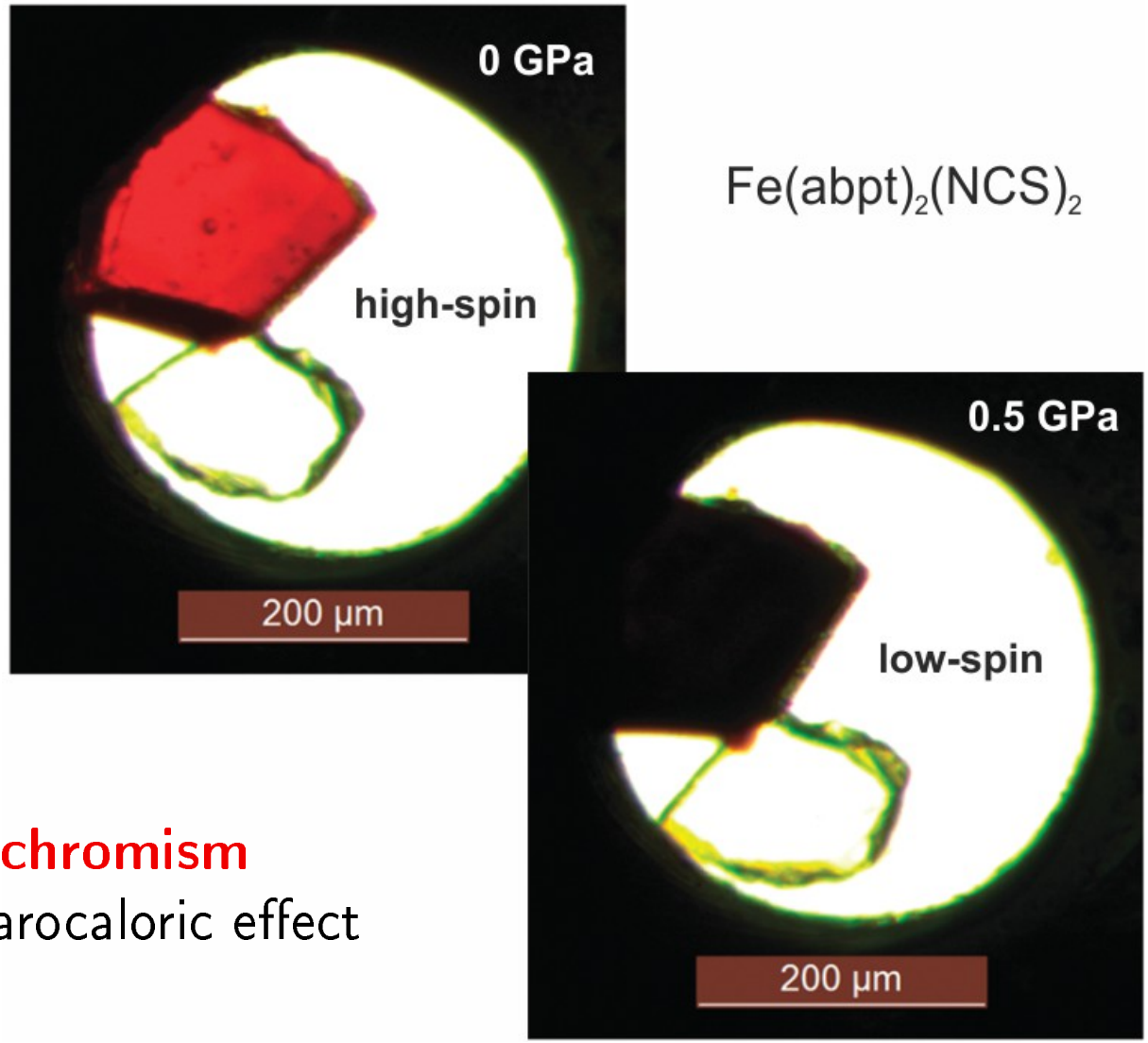
Fe^{2+} $(3d^6)$



Thermochromism

Inorg. Chem. 60, 7337 (2021)

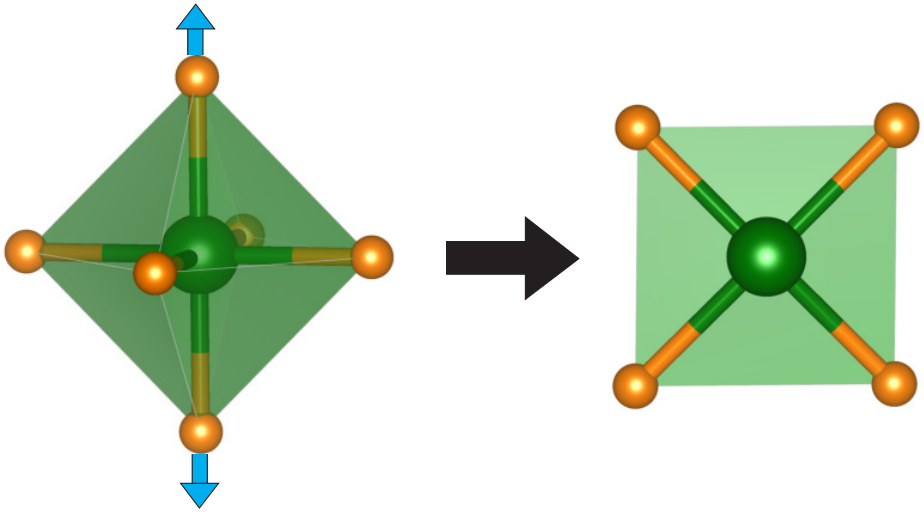
Fe^{2+} $(3d^6)$

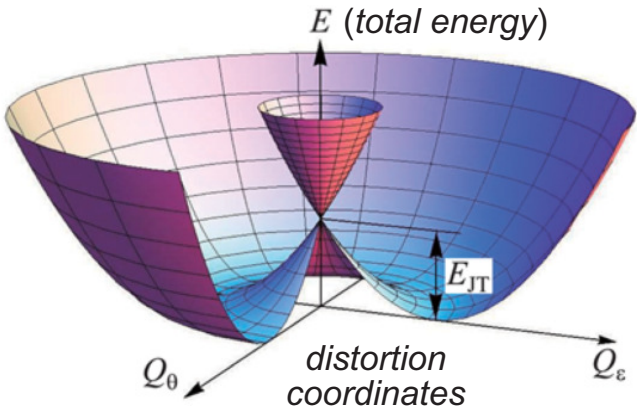


$Fe(abpt)_2(NCS)_2$

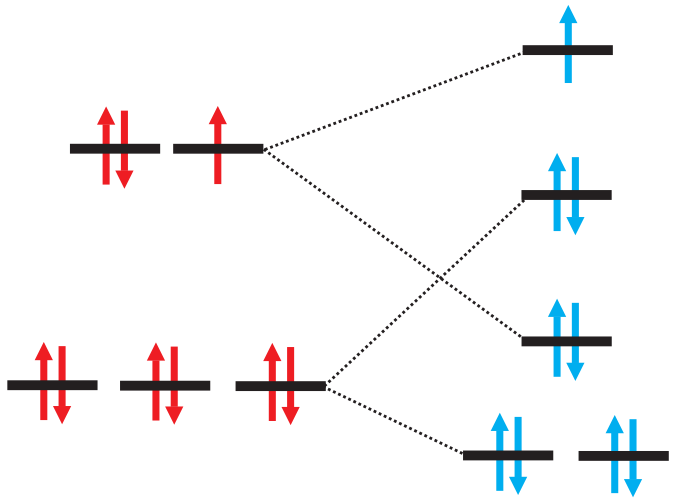
Piezochromism
and barocaloric effect

New J. Chem. 40, 2466 (2016)





$\mathbf{Cu}^{2+}$ $(3d^9)$



regular octahedron

orbitally degenerate

elongated octahedron

non-degenerate

J. Phys. Chem. A 121, 7246 (2017)