Symmetry in Condensed Matter Physics

Exercise 4. Splitting of the free-ion orbital and spin states by electric crystal fields

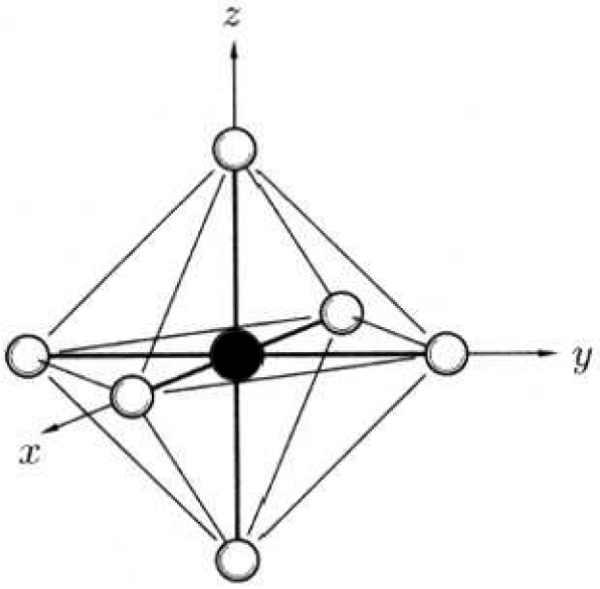
1. The rare-earth lanthanide ion Yb^{3+} ($4f^{13}$) has a ground state multiplet $^2F_{7/2}$ (L=3, S=1/2, J=7/2). Find the irreducible representations of the energy levels in a cubic crystal field of symmetry 432. What would be the difference if the symmetry was $m3m = 432 \times \bar{1}$?

2. The ground state of the vanadium V^{3+} ($3d^2$) free ion has total orbital angular momentum quantum number L=3. Show that when the ion is placed in a cubic crystal field of point symmetry $m3m$ the energy states of the d electrons split into 3 levels with symmetries T_{1g}, T_{2g}, and A_{2g}.

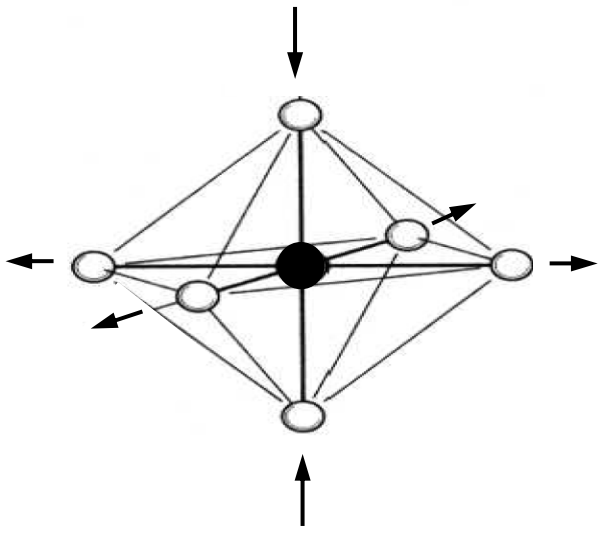
The local electric field is then altered by a transition to 422 symmetry. Calculate the splittings of the cubic states. Assuming that the ground state in cubic symmetry is the T_{1g} level, determine the infrared spectrum for the 422 symmetry. Ignore spin-orbit couplings.

3. The ground state of the titanium Ti^{3+} ($3d^1$) free ion has orbital angular momentum quantum number L=2. The ion is now placed in the centre of an Oxygen octahedron of cubic symmetry of point group $m3m$, which is then slightly distorted to tetragonal point group $4/mmm$ by compression of the octahedron along the z-axis as shown below. Find the degeneracies and symmetries of the orbital energy levels (neglect spin-orbit couplings) and determine the infrared and Raman spectra. The character table for $4/mmm$ is attached.

Transitions between orbital levels can also be probed by inelastic scattering of neutrons. Selection rules are found by analysing the matrix elements of the orbital angular momentum operator **L** between the initial and final states, $\langle \psi_2 | \mathbf{L} | \psi_1 \rangle$. For example, if the component L_z has a finite matrix element $\langle \psi_2 | L_z | \psi_1 \rangle \neq 0$ then incident neutrons with spin polarized along the z-axis can scatter inelastically with spin unchanged and excite the system from state ψ_1 to ψ_2. Using the fact that the orbital angular momentum is an axial vector (whose components L_x, L_y, L_z, transform like the rotation operators R_x, R_y, R_z, respectively) determine the spectrum of transitions accessible via neutron scattering for the Ti^{3+} ion in $4/mmm$ symmetry.



Octahedral cubic
$m3m$



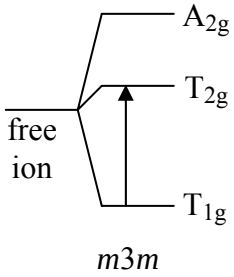
Tetragonal
$4/mmm$

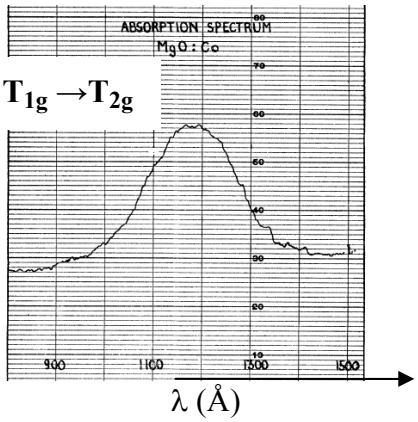
4. (harder) The ground state of the cobalt Co^{2+} ($3d^7$) free ion has orbital angular momentum quantum number L=3 according to Hund's rules. In a cubic crystal field of point group symmetry $m3m$ the orbital states of the d electrons split into 3 levels with symmetries T_{1g}, T_{2g}, A_{2g} (in this order of increasing energy).

a) Show that the $T_{1g} \rightarrow T_{2g}$ transition is <u>not</u> infrared active. Ignore spin orbit couplings.

b) However, the experimentally measured infrared absorption spectrum shows a clear absorption peak when the radiation frequency matches the $T_{1g} \rightarrow T_{2g}$ energy gap, as shown below.

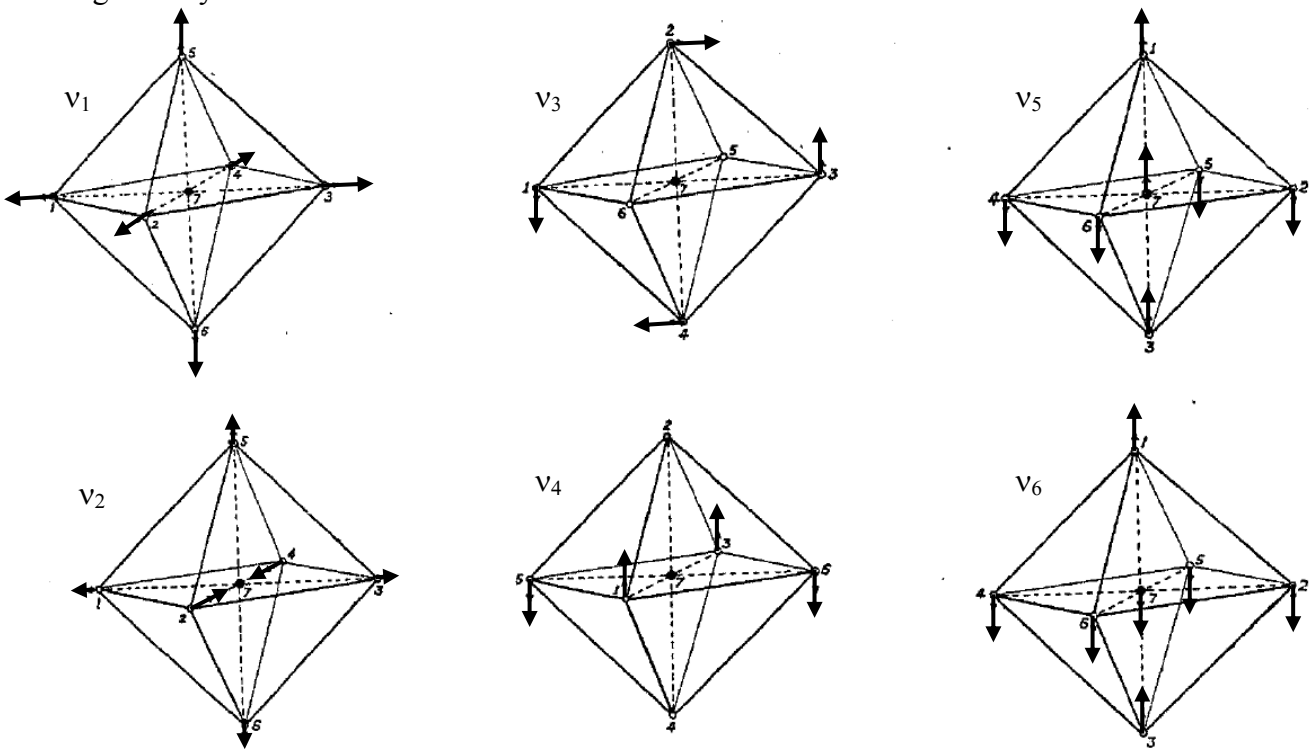
Infrared absorption spectrum in Co^{2+} ions in a cubic octahedral crystal field showing an absorption peak near the $T_{1g} \rightarrow T_{2g}$ energy gap.





This is a case when the purely electronic transition is electric-dipole disallowed, but infrared absorption can occur if simultaneously with the electronic transition a lattice vibration mode is also excited. In this case one needs to consider the *total* wavefunction of the system, i.e. the lattice part and the electronic part. The relevant matrix element for such transitions is $\langle \psi'_v \psi'_e \mid \mathbf{P} \mid \psi_v \psi_e \rangle$, where $\mathbf{P}$ is the usual polarization vector, ψ_v is the vibronic (lattice) state at rest, ψ_e is the electronic ground state, ψ'_v is the excited vibration state and ψ'_e is the excited electronic state.

What parity should a vibration mode have in order to be excited together with the electronic $T_{1g} \rightarrow T_{2g}$ transition by infrared absorption? Find the symmetries of the normal modes of vibration for an isolated CoO_6 cubic octahedron and show that there are normal modes of vibration with the appropriate symmetry to satisfy the selection rules for combined lattice excitation + electronic transition $T_{1g} \rightarrow T_{2g}$ via infrared absorption. Below is an illustration of several representative normal modes of vibration of the CoO_6 octahedron. By inspecting how those modes transform under inversion identify their parity. By considering how the modes transform under other symmetry operations of the octahedron identify which correspond to a singlet, doublet or triplet degenerate energy level and then deduce the full symmetry of each of the modes. Which of them can be excited together with the electronic transition $T_{1g} \rightarrow T_{2g}$ via infrared absorption? In the vibration mode ν_2 the two Oxygens depicted as moving towards the centre (labelled 2 and 4) are displaced twice as much as the other four Oxygens moving radially out.



Character tables which you may need.

422 (D_4)		E	2_z	4_z [2]	2_x [2]	2_d [2]	
Γ_1	A_1	1	1	1	1	1	x^2+y^2, z^2
Γ_2	A_2	1	1	1	–1	–1	z, R_z
Γ_3	B_1	1	1	–1	1	–1	$x^2–y^2$
Γ_4	B_2	1	1	–1	–1	1	xy
Γ_5	E	2	–2	0	0	0	(x, y), (xz, yz), (R_x, R_y)

$4/mmm$ (D_{4h}) = $422 \times \bar{1}$

$4mmm$ (D_{4h})		E	2_z	4_z [2]	2_x [2]	2_d [2]	$\bar{1}$	m_z	$\bar{4}_z$ [2]	m_x [2]	m_d [2]	
Γ^+_1	A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2
Γ^+_2	A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	R_z
Γ^+_3	B_{1g}	1	1	–1	1	–1	1	1	–1	1	–1	$x^2–y^2$
Γ^+_4	B_{2g}	1	1	–1	–1	1	1	1	–1	–1	1	xy
Γ^+_5	E_g	2	–2	0	0	0	2	–2	0	0	0	(xz, yz), (R_x, R_y)
Γ^-_1	A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1	
Γ^-_2	A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	z
Γ^-_3	B_{1u}	1	1	–1	1	–1	–1	–1	1	–1	1	
Γ^-_4	B_{2u}	1	1	–1	–1	1	–1	–1	1	1	–1	
Γ^-_5	E_u	2	–2	0	0	0	–2	2	0	0	0	(x, y)

432 (O)		E	3 [8]	2_z [3]	2_d [6]	4_z [6]	
Γ_1	A_1	1	1	1	1	1	$x^2+y^2+z^2 = r^2$
Γ_2	A_2	1	1	1	–1	–1	
Γ_3	E	2	–1	2	0	0	$(x^2–y^2, 3z^2–r^2)$
Γ_4	T_1	3	0	–1	–1	1	$(x, y, z), (R_x, R_y, R_z)$
Γ_5	T_2	3	0	–1	1	–1	(xy, xz, yz)

$m3m\ (O_h) \;=\; 432\times \bar{1}$

$m3m\ (O_h)$		E	3 [8]	2_z [3]	2_d [6]	4_z [6]	$\bar{1}$	$\bar{3}$ [8]	m_z [3]	m_d [6]	$\bar{4}_z$[6]	
Γ^+_1	A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2 = r^2$
Γ^+_2	A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	
Γ^+_3	E_g	2	–1	2	0	0	2	–1	2	0	0	$(x^2–y^2, 3z^2–r^2)$
Γ^+_4	T_{1g}	3	0	–1	–1	1	3	0	–1	–1	1	(R_x, R_y, R_z)
Γ^+_5	T_{2g}	3	0	–1	1	–1	3	0	–1	1	–1	(xy, xz, yz)
Γ^-_1	A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1	
Γ^-_2	A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	
Γ^-_3	E_u	2	–1	2	0	0	–2	1	–2	0	0	
Γ^-_4	T_{1u}	3	0	–1	–1	1	–3	0	1	1	–1	(x, y, z)
Γ^-_5	T_{2u}	3	0	–1	1	–1	–3	0	1	–1	1	

d–432		E	$\bar{E}$	3	$\bar{E}3$	2_z $\bar{E}2_z$	2_d $\bar{E}2_d$	4_z	$\bar{E}4_z$
Γ_1	A_1	1	1	1	1	1	1	1	1
Γ_2	A_2	1	1	1	1	1	–1	–1	–1
Γ_3	E	2	2	–1	–1	2	0	0	0
Γ_4	T_1	3	3	0	0	–1	–1	1	1
Γ_5	T_2	3	3	0	0	–1	1	–1	–1
Γ_6		2	–2	1	–1	0	0	$\sqrt{2}$	$-\sqrt{2}$
Γ_7		2	–2	1	–1	0	0	$-\sqrt{2}$	$\sqrt{2}$
Γ_8		4	–4	–1	1	0	0	0	0