Project Crystal Field
Physics 481 / Spring 2000
Professor Klaus Schulten

Problem : Magnetic Ion in Crystalline Electric Field

Consider a Ti^{3+} ion which has been inserted substitutionally into an ionic crystal lattice. The Ti^{3+} ion has one $3d$ electron and we assume that this ion is in a state belonging to the lowest energy term ^2D. This energy term[1] is labeled through the orbital angular momentum quantum number $L = 2$ and the spin quantum number $S = \frac{1}{2}$. Hence, the energy term ^2D has a $2L + 1 = 5$ fold orbital degeneracy and a $2S + 1 = 2$ fold spin degeneracy. As a result of the interaction between the ion and the electric field of the crystal lattice the orbital degeneracy of the energy term ^2D can be lifted, at least in part. Our aim in this problem is to calculate the splitting of the energy term ^2D of Ti^{3+} in a crystalline electric field with cubic symmetry. For this purpose we assume the following approximations:

(i) The ionic crystal lattice is considered as a point-charge lattice with simple cubic symmetry.

(ii) The crystalline electric field acts only on the outermost $3d$ electron of Ti^{3+}; the other electrons of Ti^{3+} are located in closed shells and therefore they are not perturbed by the crystalline field.

(iii) The $3d$ electron's wave function is

$$\psi_m(r, \theta, \varphi) \;=\; f(r) Y_{2,m}(\theta, \varphi) \;, \tag{1}$$

where r is measured from the center of Ti^{3+} which is located in the origin, and $m = \pm 2, \pm 1, 0$. The radial part of the wave function $f(r)$ is not accurately known and, therefore, the radial integrals arising in this problem

$$< r^n > \;=\; \int [f(r)]^2 r^n r^2 dr \;, \tag{2}$$

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[1]By "energy term" we mean an energy level of an atom or ion which has more than one electron. In this problem we assume that the energy terms can be labeled by the total angular momentum and by the total spin quantum numbers of the electronic system of the atom or ion.

where n is an integer, will be considered as parameters, i.e., express your final result in terms of these integrals without explicitly evaluating them. In contrast, the angular part of the wave function is precisely known and it is given by the spherical harmonics $Y_{2,m}(\theta, \varphi)$.

(iv) The electric field at $\vec{r} = (r, \theta, \varphi)$ can be approximated by the Coulomb field created by the six nearest neighbor negative ions (Fig.1); each of these ions is at a distance d from the origin and has an electric charge $-e$.

The interaction Hamiltonian between Ti^{3+} and the lattice is then given by the electrostatic potential energy of the $3d$ electron in the electric field due to the six nearest neighbor ions, i.e.,

$$V(\vec{r}) \; = \; \sum_{i=1}^{6} \frac{e^2}{|\vec{r} - \vec{R}_i|} \; . \tag{3}$$

Now, the splitting of the energy term ^2D can be obtained by diagonalizing $< \psi_{m'} | V | \psi_m >$.

(a) By means of the well-known formula

$$\frac{1}{|\vec{r} - \vec{R}|} \; = \; \sum_{l=o}^{\infty} \sum_{m=-l}^{l} \frac{r^l}{R^{l+1}} \frac{4\pi}{2l+1} Y_{l,m}^*(\Theta, \Phi) Y_{l,m}(\theta, \varphi) \; , \tag{4}$$

where $\vec{R} = (R, \Theta, \Phi)$, show that V can be expanded in a series of spherical harmonics. Then, employing the Wigner-Eckart theorem, prove that, in our case, it is sufficient to expand V up to the order $l_{max} = 4$ since other terms do not contribute to the matrix elements $< \psi_{m'} | V | \psi_m >$. Use the provided '*Mathematica*' notebook[2] to obtain an explicit form of the expansion of V up to the required order.

(b) By making the substitutions

$$\begin{aligned}
\sin\theta e^{i\varphi} \; &\rightarrow \; r_+/r = (x + iy)/r \\
\sin\theta e^{-i\varphi} \; &\rightarrow \; r_-/r = (x - iy)/r \\
\cos\theta \; &\rightarrow \; z/r
\end{aligned} \tag{5}$$

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[2] The title of the provided '*Mathematica*' notebook is `Magnetic-Ion.ma` and is located on the EWS SUN's in the directory: /work/cesn1a/phy481/phy481b0/PHYCS481/ For more details please refer to the handout "Introduction to *Mathematica*".

in the spherical harmonics in the above obtained expression of V express V through Cartesian coordinates x, y and z, i.e.,

$$r^l Y_{l,m}(\theta, \varphi) \equiv \mathbb{Y}_{l,m}(x,y,z) \ . \tag{6}$$

Employ the Wigner-Eckart theorem to prove

$$
\begin{aligned}
r^\ell < L, M'|Y_{l,m}|L, M > \ &\equiv \ < L, M'|\mathbb{Y}_{l,m}(x,y,z)|L, M > \\
&= \ C[L,l] \times < L, M'|\mathbb{Y}_{l,m}(L_x, L_y, L_z)|L, M > \tag{7}
\end{aligned}
$$

where $C[L,l]$ is a proportionality constant which is one and the same for all $m = 0, \pm 1, \ldots, \pm l$ and $M = 0, \pm 1, \ldots, \pm L$. Employing *'Mathematica'* evaluate $C[2,l]$ for those l's which appear in the expansion of V and, hence, express V in terms of operator equivalents L_i $(i = x, y, z)$.

Warning! Because the components of the angular momentum do not commute, as the spatial coordinates do, in an operator equivalent products of x, y and z have to be replaced by all the different combinations of L_x, L_y and L_z, divided by the total number of combinations.

(c) Using the provided *'Mathematica'* notebook, diagonalize V and explain how the term ^2D splits in the considered crystalline field.
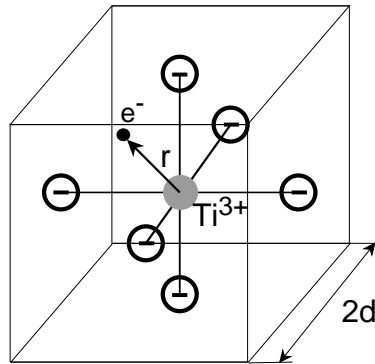

Figure 1: The Ti^{3+} ion in a sixfold cubic coordination. **r** denotes the position vector of the $3d$ electron.

   This project needs to be handed in by Friday, May 12, 2000 into the mail box of Gheorghe-Sorin Paraoan in Loomis.