

(PS3)

Point charge model calculations of crystal electric fields in the filled Skutterudite compounds

K. Takegahara¹, K. Hashimoto¹ and H. Harima²

1 - Department of Materials Science and Technology, Hirosaki University,
Hirosaki, Aomori 036-8561, Japan

2 - The Institute of Scientific and Industrial Research, Osaka University,
Ibaraki, Osaka 567-0047, Japan

The filled skutterudite RT_4X_{12} (R = rare earth; T = Fe, Ru and Os; X = P, As and Sb) crystallizes in a unique BCC structure of a space group $\text{Im} = 3 (T_h^5, \# 204)$. The atom positions are the following: R in 2a: (0, 0, 0), T in 8c: (1/4, 1/4, 1/4) and X in 24g: (0, u , v).

On the basis of a simple point charge model, we have studied the crystal electric fields (CEF). The local point symmetry of R ion is the cubic point group T_h [1]. In the T_h symmetry, the general atom positions are 24 positions, $(\pm u, \pm v, \pm w)$, $(\pm w, \pm u, \pm v)$ and $(\pm v, \pm w, \pm u)$. Due to point charges of charge qe at the 24 positions, the CEF potential is written as

$$V(\mathbf{r}) = e^2 q \left\{ \frac{1}{a^5} A_c^4 G_c^4(u, v, w) G_c^4(x, y, z) + \frac{1}{a^7} A_c^6 G_c^6(u, v, w) G_c^6(x, y, z) + \frac{1}{a^7} A_t^6 G_t^6(u, v, w) G_t^6(x, y, z) \right\}, \quad (1)$$

where a is the lattice constant and the functions G_p^l have the familiar formulas as

$$G_c^4(x, y, z) = x^4 + y^4 + z^4 - \frac{3}{5}(x^2 + y^2 + z^2)^2, \quad (2)$$

$$G_c^6(x, y, z) = x^6 + y^6 + z^6 + \frac{15}{4}(x^2 y^4 + x^2 z^4 + y^2 x^4 + y^2 z^4 + z^2 x^4 + z^2 y^4) - \frac{15}{14}(x^2 + y^2 + z^2)^3, \quad (3)$$

$$G_t^6(x, y, z) = (x^2 - y^2)(y^2 - z^2)(z^2 - x^2). \quad (4)$$

The coefficients A_p^l are calculated to be

$$A_c^4 = -\frac{175}{2(u^2 + v^2 + w^2)^{9/2}}, \quad A_c^6 = -\frac{588}{(u^2 + v^2 + w^2)^{13/2}}, \quad A_t^6 = -\frac{3465}{4(u^2 + v^2 + w^2)^{13/2}}. \quad (5)$$

Contributions from 12 positions of the nearest neighbour X ions can be calculated from Eq. (1) with $w = 0$ but the coefficients A_p^l should be in half because the positions $(u, v, \pm 0)$ give the same. Note that, if we include additional 24 general positions, $(\pm v, \pm u, \pm w)$, $(\pm u, \pm w, \pm v)$ and $(\pm w, \pm v, \pm u)$, which appear in the cubic point group O_h , we have $G_t^6(u, v, w) = 0$.

After the lattice sum for each ions, we introduce effective charges $q_i e$ ($i = \text{R, T, X}$). Under the charge neutrality condition, $q_R + 4q_T + 12q_X = 0$ with $q_R = +3$ or $+2$, we calculate CEF potential for $-1 \leq q_T \leq 1$. For $\text{PrFe}_4\text{P}_{12}$, $\text{PrRu}_4\text{P}_{12}$ and $\text{PrOs}_4\text{Sb}_{12}$, the eigenvalues and eigenfunctions of CEF potential are investigated. At $q_T^4 = -0.30 \sim -0.17$, the coefficient of the 4th order term vanishes. The ground state is $\Gamma_4^{(2)}$ for $q_T < q_T^4$ and Γ_1 for $q_T > q_T^4$ because the 4th order term is dominant. However, at a very narrow region around q_T^4 , the ground state is $\Gamma_4^{(1)}$. The calculated results are compared with the recent experimental analysis of $\text{PrOs}_4\text{Sb}_{12}$ [2].

[1] K. Takegahara *et al.*: J. Phys. Soc. Jpn. 70 (2001) 1190. Addenda: *ibid.* 70 (2001) 3468.

Errata: *ibid.* 71 (2002) 372.

[2] M. Kohgi *et al.*: J. Phys. Soc. Jpn. 72 (2003) 1002.