



94

ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ
ДУБНА

904/2-81

23/II-81

E17-80-725

S.Adam, Gh.Adam, A.Corciovei*

EFFECTIVE ONE-PARTICLE
CRYSTAL FIELD POTENTIALS
IN THE POINT CHARGE APPROXIMATION

Submitted to "physica status solidi"

* Section of Fundamental Physics, Institute of Physics and Nuclear Engineering, Bucharest, Romania.

1980

1. INTRODUCTION

The one-particle effects accounted for in the frame of the crystal field theory are described starting with the basic assumption of the legitimacy of replacing the spatially extended ions by point charges. The point charge approximation is then supplemented ^{/1-5/} by the hypothesis of the Coulombian character of the interatomic forces in the crystal. The resulting crystal field parameters are generally unrealistic and several supplementary effects have been investigated to improve the theory (see, e.g., ref. ^{/6/} and references quoted therein). Among them, unanimously accepted and included in the model is the screening of the magnetic f electrons by the outer shells of the corresponding ions ^{/7/}.

In spite of the limitations of the model, this was extensively used for the interpretation of the experimental data both in nonmetallic ^{/8-18/} and intermetallic compounds. In fact, for the metallic systems, the actual interatomic potentials are known to strongly deviate from the Coulombian behaviour, and to vary significantly from a compound to another ^{/19/}. It appears therefore justified a study concerning the deviation of the crystal field Hamiltonian which, while adopting the point charge approximation, is free from special assumptions on the spatial behaviour of the interatomic forces. Recently, Duthie and Heine ^{/20/} derived results for the crystal field coefficients under the hypothesis of arbitrary interatomic potentials. However, their starting expressions for the crystal field coefficients were taken from a paper by Hutchings ^{/3/}, who used both the point charge approximation and the hypothesis of the Coulombian character of the interatomic forces. In the present paper we show that the crystal field Hamiltonian of a system of point charges, which interact through arbitrary effective potentials, is obtained as a usual, symmetry dependent, linear combination of spherical harmonics, whose coefficients are, however, different from those given in ref. ^{/3/}. Of course, when postulating the $1/R$ behaviour of the interatomic forces, these coefficients reduce to the known results.

This paper is organized as follows. In section 2, starting from the more crude results of our previous papers ^{/21,22/}, we develop a quite general symmetrization technique which

yields an expression for the crystal field potential that is manifestly invariant to the point group of the given crystal site. Then this procedure is particularized in sections 3 and 4 to cubic and respectively hexagonal structures. The main new results brought by the present study are summarized in section 5.

2. SYMMETRIZED EXPRESSIONS OF THE CRYSTAL FIELD POTENTIALS

Let \mathcal{G} be the point group of the ionic site of interest and $G, i=1,2,\dots,N$, its elements. Let $v(\vec{R}_j)$ be the effective one-particle potential which characterizes the interaction between the reference ion taken as origin and the neighbouring ion located at \vec{R}_j . The invariance of the crystal under \mathcal{G} implies

$$v(G_i \vec{R}_j) = v(\vec{R}_j), \quad G_i \in \mathcal{G}, \quad i=1,2,\dots,N, \quad (1)$$

for every \vec{R}_j site, $j=1,2,\dots$.

The one-particle crystal field potential acting on an f (or d) electron found at the site r in an incomplete f (respectively d) shell of the reference ion is obtained from

$$V(\vec{r}) = (e/4\pi\epsilon_0) \sum_j Q_j v(\vec{R}_j - \vec{r}), \quad (2)$$

where the summation index j runs over all the lattice sites and the factor $(4\pi\epsilon_0)^{-1}$ is specific for the International System of Units. Here e is the electron charge, while Q_j denotes the effective charge of the ion located at \vec{R}_j . Taking into account Eq. (1), alternative expressions for $V(\vec{r})$ are given by

$$V(\vec{r}) = (e/4\pi\epsilon_0) \sum_j Q_j v(G_i \vec{R}_j - \vec{r}), \quad G_i \in \mathcal{G}, \quad i=1,\dots,N. \quad (3)$$

The existence of N equivalent expressions (3) of $V(\vec{r})$ allows us to redefine it as the N -th fraction of their sum. This provides us with an expression of $V(\vec{r})$ which is manifestly invariant under the point group \mathcal{G} , namely,

$$V(\vec{r}) = (e/4\pi\epsilon_0) \sum_j Q_j W(\vec{R}_j, \vec{r}), \quad (4)$$

where

$$W(\vec{R}_j, \vec{r}) = N^{-1} \sum_{i=1}^N v(G_i \vec{R}_j - \vec{r}). \quad (5)$$

Now, with the usual crystal field hypothesis,

$$x \ll X_j, \quad y \ll Y_j, \quad z \ll Z_j, \quad (6)$$

where $\vec{r}=(x,y,z)$, $\vec{R}_j=(X_j,Y_j,Z_j)$, we can expand $v(G_i \vec{R}_j - \vec{r})$ in a convergent Taylor series around $G_i \vec{R}_j$ and get

$$W(\vec{R}_j, \vec{r}) = \sum_{p=0}^{\infty} \frac{r^p}{p!} N^{-1} \sum_{i=1}^N G_i \left(k \frac{\partial}{\partial X_j} + \ell \frac{\partial}{\partial Y_j} + m \frac{\partial}{\partial Z_j} \right)^p v(\vec{R}_j). \quad (7)$$

Here, $r=|\vec{r}|$, while $k=x/r$, $\ell=y/r$ and $m=z/r$ denote the direction cosines of the vector \vec{r} .

Once the point group \mathcal{G} was specified, our task is to put the quantity $W(\vec{R}_j, \vec{r})$, Eq. (7), in a form which is appropriate for the crystal field theory. In this paper we use the notation of Bradley and Cracknell²³, which we find the most convenient for our purposes: the international notation for the symbols of the crystallographic point groups and the Schönflies notation for the individual elements of a given point group.

If \mathcal{G} contains the inversion I we can write it as a direct product,

$$\mathcal{G} = \mathcal{H} \otimes \bar{1}, \quad (8)$$

where $\bar{1} = (E, I)$ is the inversion group, and we have

$$N = 2M, \quad (9)$$

where M is the order of the invariant subgroup \mathcal{H} . Using (3) and (9) in (7), we get nonvanishing contributions to the sum over p only for $p=2q$, $q=0,1,2,\dots$, therefore in this case,

$$W(\vec{R}_j, \vec{r}) = \sum_{q=0}^{\infty} \frac{r^{2q}}{(2q)!} M^{-1} \sum_{i=1}^M G_i \left(k \frac{\partial}{\partial X_j} + \ell \frac{\partial}{\partial Y_j} + m \frac{\partial}{\partial Z_j} \right)^{2q} v(\vec{R}_j), \quad (10)$$

$G_i \in \mathcal{H}.$

In the following, we shall consider explicitly two cases which correspond to the most frequently investigated crystal structures. The first in the case of cubic crystalline systems, when

$$\mathcal{G} = m\bar{3}m = 432 \otimes \bar{1}, \quad \mathcal{H} = 432, \quad M = 24, \quad (11)$$

while the second is that of the hexagonal crystalline systems, when

$$\mathcal{G} = 6/mmm = 6m\bar{m}m \otimes \bar{1}, \quad \mathcal{H} = 6m\bar{m}m, \quad M = 12. \quad (12)$$

3. EFFECTIVE ONE-PARTICLE CRYSTAL FIELD POTENTIALS IN CUBIC CRYSTALS

Taking into account Eq. (11), the sum over i in Eq. (10) can be factorized as

$$\sum_{i=1}^{24} G_i = (E + \sigma_v^x)(E + C_3 + C_3')(E + \sigma_h^x + \sigma_h^y + \sigma_h^z). \quad (13)$$

Introducing in (10), we get after long but straightforward algebra,

$$\begin{aligned} W(\vec{R}_j, \vec{r}) = & \frac{1}{24} \sum_{q=0}^{\infty} \frac{r^{2q}}{(2q)!} \sum_{\kappa=0}^{2q} \sum_{\mu=0}^{\kappa} C_{2q}^{\kappa} C_{\kappa}^{\mu} [1 + (-1)^{2q-\kappa} (-1)^{\kappa-\mu} + \\ & + (-1)^{\mu}] k^{\mu} \ell^{\kappa-\mu} m^{2q-\kappa} [\partial^{2q} / (\partial X_j^{\mu} \partial Y_j^{\kappa-\mu} \partial Z_j^{2q-\kappa}) + \\ & + \partial^{2q} / (\partial X_j^{\mu} \partial Y_j^{2q-\kappa} \partial Z_j^{\kappa-\mu}) + \partial^{2q} / (\partial X_j^{\kappa-\mu} \partial Y_j^{\mu} \partial Z_j^{2q-\sigma}) + \\ & + \partial^{2q} / (\partial X_j^{\kappa-\mu} \partial Y_j^{2q-\kappa} \partial Z_j^{\mu}) + \partial^{2q} / (\partial X_j^{2q-\kappa} \partial Y_j^{\mu} \partial Z_j^{\kappa-\mu}) + \\ & + \partial^{2q} / (\partial X_j^{2q-\kappa} \partial Y_j^{\kappa-\mu} \partial Z_j^{\mu})] v(\vec{R}_j). \end{aligned} \quad (14)$$

In this equation,

$$1 + (-1)^{2q-\kappa} + (-1)^{\kappa-\mu} + (-1)^{\mu} = \begin{cases} 4 & \text{iff } \kappa = 2\lambda \text{ and } \mu = 2\nu, \\ 0 & \text{otherwise,} \end{cases} \quad (15)$$

therefore we have finally,

$$\begin{aligned} W(\vec{R}_j, \vec{r}) = & \frac{1}{6} \sum_{q=0}^{\infty} \frac{r^{2q}}{(2q)!} \sum_{\lambda=0}^q \sum_{\nu=0}^{\lambda} C_{2q}^{2\lambda} C_{2\lambda}^{2\nu} k^{2\nu} \ell^{2(\lambda-\nu)} m^{2(q-\lambda)} \times \\ & \times [\partial^{2q} / (\partial X_j^{2\nu} \partial Y_j^{2(\lambda-\nu)} \partial Z_j^{2(q-\lambda)}) + \partial^{2q} / (\partial X_j^{2\nu} \partial Y_j^{2(q-\lambda)} \partial Z_j^{2(\lambda-\nu)}) + \\ & + \partial^{2q} / (\partial X_j^{2(\lambda-\nu)} \partial Y_j^{2\nu} \partial Z_j^{2(q-\lambda)}) + \partial^{2q} / (\partial X_j^{2(\lambda-\nu)} \partial Y_j^{2(q-\lambda)} \partial Z_j^{2\nu}) \\ & + \partial^{2q} / (\partial X_j^{2(q-\lambda)} \partial Y_j^{2\nu} \partial Z_j^{2(\lambda-\nu)}) + \partial^{2q} / (\partial X_j^{2(q-\lambda)} \partial Y_j^{2(\lambda-\nu)} \partial Z_j^{2\nu})] v(\vec{R}_j). \end{aligned} \quad (16)$$

Thus, the most general expression of the one-particle effective potential in cubic crystals is given by Eq. (4) with $W(\vec{R}_j, r)$ found from Eq. (16).

As it is well-known^{1-5/}, only some terms of this expression are relevant for the crystal field Hamiltonian. In order to rule out the unnecessary quantities, we have to factorize out the electronic and ionic contributions. As a result of the factorization, we get an expression of the form

$$W(\vec{R}_j, r) = \sum_{q=0}^{\infty} \frac{r^{2q}}{(2q+1)!} \Delta_j^q v(\vec{R}_j) + \sum_{n=2}^{\infty} p_{2n}(k, \ell, m) \times \sum_{q=0}^{\infty} \frac{r^{2(n+q)}}{(2n+2q)!} c_{2n+2q, 2n} \Delta_j^q P_{2n}(K_j, L_j, M_j), \quad (17)$$

where Δ_j is the Laplacian acting on the co-ordinates of the j -th ionic site, $p_{2n}(k, \ell, m)$ are linear combinations of unnormalized tesseral harmonics of the order $2n$, $P_{2n}(K_j, L_j, M_j)$ are homogeneous linear combinations of partial derivatives of the order $2n$ of $v(\vec{R}_j)$, $c_{2n+2q, 2n}$ are some numerical coefficients. Finally, $K_j = X_j/R_j$, $L_j = Y_j/R_j$, $M_j = Z_j/R_j$ denote the direction cosines of the vector \vec{R}_j .

Nonvanishing matrix elements are obtained only from the terms $p_4(k, \ell, m)$ and $p_6(k, \ell, m)$, and therefore the relevant crystal field potential is given by

$$V_{cf}(\vec{r}) = A_4(r) p_4(k, \ell, m) + A_6(r) p_6(k, \ell, m), \quad (18)$$

where, as usual (Hutchings^{3/}),

$$p_4(k, \ell, m) = k^4 + \ell^4 + m^4 - 3/5, \quad (19a)$$

$$p_6(k, \ell, m) = k^6 + \ell^6 + m^6 + (15/4)(k^4 \ell^2 + \ell^4 m^2 + m^4 k^2 + k^2 \ell^4 + \ell^2 m^4 + m^2 k^4) - 15/14, \quad (19b)$$

while

$$A_4(r) = \frac{e}{4\pi\epsilon_0} \sum_{q=0}^{\infty} \frac{r^{4+2q}}{(4+2q)!} c_{4+2q, 4} \sum_j Q_j \Delta_j^q P_4(K_j, L_j, M_j), \quad (20a)$$

$$A_6(r) = \frac{e}{4\pi\epsilon_0} \sum_{q=0}^{\infty} \frac{r^{6+2q}}{(6+2q)!} c_{6+2q, 6} \sum_j Q_j \Delta_j^q P_6(K_j, L_j, M_j). \quad (20b)$$

Here,

$$P_4(K_j, L_j, M_j) = \left(\frac{\partial^4}{\partial X_j^4} + \frac{\partial^4}{\partial Y_j^4} + \frac{\partial^4}{\partial Z_j^4} - \frac{3}{5} \Delta_j^2 \right) v(\vec{R}_j), \quad (21a)$$

$$P_6(K_j, L_j, M_j) = \left[\frac{\partial^6}{\partial X_j^6} + \frac{\partial^6}{\partial Y_j^6} + \frac{\partial^6}{\partial Z_j^6} - \frac{15}{4} \left(\frac{\partial^6}{\partial X_j^4 \partial Y_j^2} + \frac{\partial^6}{\partial Y_j^4 \partial Z_j^2} + \frac{\partial^6}{\partial Z_j^4 \partial X_j^2} + \frac{\partial^6}{\partial X_j^2 \partial Y_j^4} + \frac{\partial^6}{\partial Y_j^2 \partial Z_j^4} + \frac{\partial^6}{\partial Z_j^2 \partial X_j^4} \right) - \frac{15}{14} \Delta_j^3 \right] v(\vec{R}_j).$$

The coefficients $c_{2n+2q, 2n}$, $n=2,3$, characterize the contributions to the crystal field potential of the terms of the order $2(n+q)$, $n+q=2,3,\dots$, of the power series development (16). They are obtained after very long and intricate calculations. The lowest order coefficients are respectively

$$c_{4,4} = 5/6, \quad c_{6,4} = 25/22, \quad c_{6,6} = 56/33. \quad (22)$$

Under the hypothesis of the Coulombian interatomic forces,

$$\Delta_j^q P_{2n}(K_j, L_j, M_j) = 0, \quad n=2,3; \quad q=1,2,\dots, \quad (23)$$

and the sums (20) reduce to the term $q=0$. Further, we get

$$P_4(K_j, L_j, M_j) = K_j^4 + L_j^4 + M_j^4 - 3/5, \quad (24a)$$

$$P_6(K_j, L_j, M_j) = K_j^6 + L_j^6 + M_j^6 + (15/4)(K_j^4 L_j^2 + L_j^4 M_j^2 + M_j^4 K_j^2 + K_j^2 L_j^4 + L_j^2 M_j^4 + M_j^2 K_j^4) - 15/14, \quad (24b)$$

therefore Eqs. (20) reduce to the usual crystal field coefficients for cubic compounds,

$$A_4(r) = \frac{e}{4\pi\epsilon_0} \frac{r^4}{4!} \frac{5}{6} \sum_j Q_j (K_j^4 + L_j^4 + M_j^4 - \frac{3}{5}), \quad (25a)$$

$$A_6(r) = \frac{e}{4\pi\epsilon_0} \frac{r^6}{6!} \frac{56}{33} \sum_j Q_j \left[K_j^6 + L_j^6 + M_j^6 + \frac{15}{4} (K_j^4 L_j^2 + L_j^4 M_j^2 + M_j^4 K_j^2 + K_j^2 L_j^4 + L_j^2 M_j^4 + M_j^2 K_j^4) - \frac{15}{14} \right]. \quad (25b)$$

4. EFFECTIVE ONE-PARTICLE CRYSTAL FIELD POTENTIALS IN HEXAGONAL CRYSTALS

Taking into account Eq. (12), the sum over i in Eq. (10) can be factorized as

$$\sum_{i=1}^{12} G_i = (E + C_6 + C_3)(E + \sigma_v^y)(E + \sigma_h^z), \quad (26)$$

and we get from (10) and (1),

$$\begin{aligned} W(\vec{R}_j, \vec{r}) &= \frac{1}{3} \sum_{q=0}^{\infty} \frac{r^{2q}}{(2q)!} \sum_{\lambda=0}^q \sum_{\mu=0}^{\lambda} C_{2q}^{2\lambda} C_{2\lambda}^{2\mu} k^{2\mu} \ell^{2(\lambda-\mu)} m^{2(q-\lambda)} \times \\ &\times \left\{ \frac{\partial^{2\lambda}}{\partial X_j^{2\mu} \partial Y_j^{2(\lambda-\mu)}} + \frac{1}{2^{2\lambda-1}} \sum_{\nu=0}^{\lambda-\mu} C_{2(\lambda-\mu)}^{2\nu} \sum_{\sigma=0}^{\mu} 3^{\mu+\nu-\sigma} C_{2\mu}^{2\sigma} \times \right. \\ &\times \frac{\partial^{2\lambda}}{\partial X_j^{2(\nu+\sigma)} \partial Y_j^{2(\lambda-\nu-\sigma)}} - \frac{1}{\lambda^{2\lambda-1}} \sum_{\nu=1}^{\lambda-\mu} C_{2(\lambda-\mu)}^{2\nu-1} \sum_{\sigma=0}^{\mu-1} 3^{\mu+\nu-\sigma-1} C_{2\mu}^{2\sigma+1} \times \\ &\times \left. \frac{\partial^{2\lambda}}{\partial X_j^{2(\nu+\sigma)} \partial Y_j^{2(\lambda-\nu-\sigma)}} \right\} \frac{\partial^{2(q-\lambda)}}{\partial Z_j^{2(q-\lambda)}} v(\vec{R}_j). \end{aligned} \quad (27)$$

Similar to the case of cubic crystals, it is necessary to factorize out the electronic and the ionic contributions to the effective potential. Performing this factorization and ruling out the contributions whose matrix elements vanish identically, we get the relevant expression of the crystal field potential as,

$$\begin{aligned} V_{cf}(\vec{r}) &= A_{20}(r) p_{20}(k, \ell, m) + A_{40}(r) p_{40}(k, \ell, m) + \\ &+ A_{60}(r) p_{60}(k, \ell, m) + A_{66}(r) p_{66}(k, \ell, m). \end{aligned} \quad (28)$$

Here, $p_{nq}(k, \ell, m)$ denote unnormalized tesseral harmonics, given respectively by

$$p_{20}(k, \ell, m) = 3m^2 - 1, \quad (29a)$$

$$p_{40}(k, \ell, m) = 35m^4 - 30m^2 + 3, \quad (29b)$$

$$p_{60}(k, \ell, m) = 231m^6 - 315m^4 + 105m^2 - 5, \quad (29c)$$

$$p_{66}(k, \ell, m) = k^6 - 15k^4\ell^2 + 15k^2\ell^4 - \ell^6, \quad (29d)$$

while

$$A_{20}(r) = \frac{e}{4\pi\epsilon_0} \sum_{q=0}^{\infty} \frac{r^{2+2q}}{(2+2q)!} c_{2+2q,2}^{\circ} \sum_j Q_j \Delta_j^q P_{20}(K_j, L_j, M_j), \quad (30a)$$

$$A_{40}(r) = \frac{e}{4\pi\epsilon_0} \sum_{q=0}^{\infty} \frac{r^{4+2q}}{(4+2q)!} c_{4+2q,4}^{\circ} \sum_j Q_j \Delta_j^q P_{40}(K_j, L_j, M_j), \quad (30b)$$

$$A_{60}(r) = \frac{e}{4\pi\epsilon_0} \sum_{q=0}^{\infty} \frac{r^{6+2q}}{(6+2q)!} c_{6+2q,6}^{\circ} \sum_j Q_j \Delta_j^q P_{60}(K_j, L_j, M_j), \quad (30c)$$

$$A_{66}(r) = \frac{e}{4\pi\epsilon_0} \sum_{q=0}^{\infty} \frac{r^{6+2q}}{(6+2q)!} c_{6+2q,6}^6 \sum_j Q_j \Delta_j^q P_{66}(K_j, L_j, M_j). \quad (30d)$$

In Eqs. (30), the characteristic contributions coming from the j -th ionic site to the crystal field potential are given by

$$P_{20}(K_j, L_j, M_j) = (3 \frac{\partial^2}{\partial Z_j^2} - \Delta_j) v(\vec{R}_j), \quad (31a)$$

$$P_{40}(K_j, L_j, M_j) = (35 \frac{\partial^4}{\partial Z_j^4} - 30 \frac{\partial^2}{\partial Z_j^2} \Delta_j + 3\Delta_j^2) v(\vec{R}_j), \quad (31b)$$

$$P_{60}(K_j, L_j, M_j) = (231 \frac{\partial^6}{\partial Z_j^6} - 315 \frac{\partial^4}{\partial Z_j^4} \Delta_j + 105 \frac{\partial^2}{\partial Z_j^2} \Delta_j^2 - 5\Delta_j^3) v(\vec{R}_j), \quad (31c)$$

$$P_{66}(K_j, L_j, M_j) = (\frac{\partial^6}{\partial X_j^6} - 15 \frac{\partial^6}{\partial X_j^4 \partial Y_j^2} + 15 \frac{\partial^6}{\partial X_j^2 \partial Y_j^4} - \frac{\partial^6}{\partial Y_j^6}) v(\vec{R}_j). \quad (31d)$$

Further, the coefficients $c_{2n+2q,2n}^a$ characterize the contributions to the crystal field potential of the terms of orders $2(n+q)$, $n+q=1, 2, 3, \dots$, of the power series development (27). Once again, the calculation of these coefficients is a difficult task, which we have accomplished for the lowest orders only. We have,

$$\begin{aligned} c_{2,2}^{\circ} &= 1/6, & c_{4,2}^{\circ} &= 1/7, & c_{6,2}^{\circ} &= 5/42, \\ c_{4,4}^{\circ} &= 1/280, & c_{6,4}^{\circ} &= 3/616, \\ c_{6,6}^{\circ} &= 1/3696, & c_{6,6}^6 &= 1/32. \end{aligned} \quad (32)$$

Under the hypothesis of Coulombian interatomic forces,

$$\Delta_j^q P_{2n,s}(K_j, L_j, M_j) = 0, \quad n=1,2,3, \quad s=0,6, \quad q=1,2,\dots, \quad (33)$$

and the sums (29) reduce to the term $q=0$. In this case, we get

$$P_{20}(K_j, L_j, M_j) = 3M_j^2 - 1, \quad (34a)$$

$$P_{40}(K_j, L_j, M_j) = 35M_j^4 - 30M_j^2 + 3, \quad (34b)$$

$$P_{60}(K_j, L_j, M_j) = 231M_j^6 - 315M_j^4 + 105M_j^2 - 5, \quad (34c)$$

$$P_{66}(K_j, L_j, M_j) = K_j^6 - 15K_j^4 L_j^2 + 15K_j^2 L_j^4 - L_j^6, \quad (34d)$$

and the expressions of the crystal field coefficients become the usual ones,

$$A_{20}(r) = \frac{e}{4\pi\epsilon_0} \frac{r^2}{2!} \frac{1}{6} \sum_j Q_j (3M_j^2 - 1), \quad (35a)$$

$$A_{40}(r) = \frac{e}{4\pi\epsilon_0} \frac{r^4}{4!} \frac{1}{280} \sum_j Q_j (35M_j^4 - 30M_j^2 + 3), \quad (35b)$$

$$A_{60}(r) = \frac{e}{4\pi\epsilon_0} \frac{r^6}{6!} \frac{1}{3696} \sum_j Q_j (231M_j^6 - 315M_j^4 + 105M_j^2 - 5), \quad (35c)$$

$$A_{66}(r) = \frac{e}{4\pi\epsilon_0} \frac{r^6}{6!} \frac{1}{32} \sum_j Q_j (K_j^6 - 15K_j^4 L_j^2 + 15K_j^2 L_j^4 - L_j^6). \quad (35d)$$

5. CONCLUDING REMARKS

In this paper we have derived, in the frame of the point charge approximation, the most general form of the one-particle crystal field potentials for cubic and hexagonal crystals.

In order to accomplish this task, it was necessary to devise an alternative approach to the derivation of the crystal field Hamiltonian. This is based on the possibility of writing the potential acting on the f (or d) electrons of the incomplete shells of the ions of interest in the form (4), which is manifestly invariant to the point group of the given crystal site.

The final results, Eqs. (18) and (28) respectively, show that the parametric expression of the crystal field potential in terms of spherical (tesseral) harmonics is the usual one. However, the coefficients of these harmonics are given by expressions, Eqs. (20) and (30) respectively, which consist of series of powers r^n rather than of single r^n terms as in the hypothesis of Coulomb interatomic forces, Eqs. (25) and (35), respectively.

It is interesting to establish the connection between the present results and those reported in two recent papers. On the one hand, in a theoretical paper, Duthie and Heine^{/20/} calculated the crystal field coefficients in cubic compounds allowing for realistic interionic potentials, but starting from expressions which are essentially equivalent to the consideration of the term $q=0$ only of Eq. (20). In order to settle the reliability of this approximation, a study of the consequences emerging from the use of the complete expressions (20) is necessary. On the other hand, in an experimental paper, Devine and Berthier^{/24/} starting with the usual picture offered by Eqs. (25) and (35), established experimental values which they called expectation values $\langle r^4 \rangle$ and $\langle r^6 \rangle$ for 4f electrons across the rare earth series. The comparison with theoretically calculated values showed a systematic discrepancy between theory and experiment for $\langle r^4 \rangle$, while for $\langle r^6 \rangle$ the considerable uncertainty in the experimental data did not allow definite inferences. The present paper sheds new light on the significance of the experimental data reported as $\langle r^4 \rangle$ and $\langle r^6 \rangle$ values in^{/24/}. Indeed, Eqs. (20) and (30) show that these data correspond in fact to expressions consisting of series of powers $\langle r^n \rangle$ rather than to pure $\langle r^4 \rangle$ or $\langle r^6 \rangle$ values, hence the direct comparison with $\langle r^4 \rangle$ and $\langle r^6 \rangle$ theoretical values obtained from atomic calculations has to be regarded with caution. A calculation starting with the present expressions for the crystal field potentials and with $v(R)$ taken from reference^{/20/} should permit a comparison of physically equivalent quantities. Quantitative answers to the questions raised by the above considerations are planned to be reported in a future paper.

REFERENCES

1. Ballhausen C.J. Introduction to Ligand Field Theory. McGraw-Hill, New York, 1962.
2. Sachs M. Solid State Theory. McGraw-Hill, New York, 1963, chap.4.

3. Hutchings M.T. In: Solid State Physics (F.Seitz, D.Turnbull, eds.), Academic Press, New York, 1964, vol.16, pp.227-272.
4. Abragam A., Bleaney B. Electron Paramagnetic Resonance of Transition Ions. Clarendon Press, Oxford, 1970, part III.
5. Eremenko V.V. Vvedenie v opticheskuyu spektroskopiyu magnetikov. "Naukova Dumka", Kiev, 1975.
6. Faucher M., Caro P. J.Chem.Phys., 1977, 66, p.1273.
7. Freeman A.J., Watson R.E. Phys.Rev., 1963, 127, p.2058.
8. Furrer A., Hälgl V. J.Phys.C: Solid State Phys., 1976, 9, p.3499.
9. Gomathy V., Basu C., Ghosh U.S. phys. stat.sol.(b), 1978, 86, p.379.
10. De Wijn H.W., Van Diepen A.M., Buschow K.H.J. Phys.Rev., 1973, B7, p.524.
11. Buschow K.H.J., Van Diepen A.M., De Wijn H.W. Solid State Commun., 1974, 15, p.903.
12. Greedan J.E., Rao V.U.S. Solid State Chem., 1972, 6, p.387.
13. Sankar S.G. et al. Phys.Rev., 1975, B11, p.435.
14. Furrer A. J.Phys.C: Solid State Phys., 1975, 8, p.824.
15. Porcher P., Caro P. J.Chem.Phys., 1976, 65, p.89.
16. Keller G., Dixon J.M. J.Phys.F: Metal Phys., 1976, 6, p.819.
17. Maeda H. phys.stat.sol.(a), 1978, 45, p.445.
18. Malik S.K., Wallace W.E., Vijayaraghavan R. Phys.Rev., 1979, B19, p.1671.
19. Torrens I.M. Interatomic Potentials. Academic Press, New York, 1972.
20. Duthie J.C., Heine V. J.Phys.F: Metal Phys., 1979, 9, p.1349.
21. Adam S., Adam Gh., Corciovei A. Rev.Roum.Phys., 1977, 22, p.39.
22. Adam S., Adam Gh. Rev.Roum.Phys., 1977, 22, p.1063.
23. Bradley C.J., Cracknell A.P. The Mathematical Theory of Symmetry in Solids: Representation Theory for Point Groups and Space Groups. Clarendon Press, Oxford, 1972.
24. Devine R.A.B., Berthier Y. Solid State Commun., 1978, 26, p.315.

Received by Publishing Department
on November 10, 1980.