The Thomas–Fermi Type Screening of the Crystal Field Multipole Moments

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Using a nonintegral expansion method of screened potentials about a displaced center (by a) the intrinsic crystal-field terms generated by the point charge, dipole, and quadrupole moments of a ligand have been quantitatively estimated. The calculation has been performed within the Thomas–Fermi model for the screening radius $1/\lambda \geq a/3$. In contrast to an almost total attenuation of the monopole component (of no contribution to the crystal-field splitting) the screening efficiency for higher crystal-field terms regularly drops. The screening factor for the fourth-order terms does not exceed 0.5 and that for the sixth-order, 0.3. In the case of the second-order crystal-field terms a particular situation is observed. Their screening factor for the point-charge potential reaches 0.6 for $\lambda a = 3$ but contributions generated by the dipole and quadrupole components are several times enhanced. This fact may explain some interpretation difficulties occurring often in the case of the second-order parameters and concerning both their magnitude and sign. © 1996 Academic Press, Inc.

INTRODUCTION

Both the parameterization of the crystal-field potential and the quantitative expressions for the parameters within the point-charge model are derived from expansion of a monopole (the point charge) potential about a displaced center. This multipole expansion holds a more general meaning and is commonly used for both phenomenological and *ab initio* parameterizations of generalized crystal-field potentials. Analogous expansions for other potentials, e.g., for higher multipoles, bare or screened, are not easily available in a compact direct form (1) which makes even a qualitative recognition of the shielding role of conduction electrons in the crystal-field effect difficult. Up to now, there is a symptomatic partition of the opinions among crystal-field model users about this role—from attributing them a minimal shielding role (2, 3) to a strong anti-shielding one, reversing the sign of the simple point-charge model parameters (4, 5).

In the present paper some quantitative estimations of the screening effect of the crystal-field potential generated by the three basic multipoles (monopole, dipole, and quadrupole), within the frame of the Thomas–Fermi model, are presented using a nonintegral expansion method (6) of $f(R)Y_L^M(\theta, \phi)$ functions about a displaced center. The results are given directly in the real coordinate space which is convenient from the crystal-field theory point of view whereas the approaches preferred by the solid state physicists, based on the dielectric constant formalism, are given in the Fourier representation (7, 8).

The estimation has been carried out for the screening radius $1/\lambda \geq a/3$, where λ is the screening constant and a the distance between the neighboring lattice sites or between the central atom (ion) and its ligand. For the smallest value of the considered screening radius ($1/\lambda = a/3$) an almost complete attenuation of the spherically symmetric term of the ligand-field potential is observed. As a matter of fact, the spherically symmetric potential about the central atom generated by a point charge of the ligand (Ze) has then the form $(Ze/r)\exp(-3)$, where r is the distance from the central atom.

A rigid linear system (central atom–ligand) is considered in the paper. The corresponding *intrinsic* crystal-field parameters can be calculated by averaging the obtained potentials over the radial distribution of unpaired electrons of the central atom.

THE NONINTEGRAL EXPANSION METHOD OF $f(R)Y_L^M(\theta, \phi)$ FUNCTIONS ABOUT A DISPLACED CENTER

1. Translational Transformation of the Bare Multipole Moments

The nonintegral expansion method of $f(R)Y_L^M(\theta, \phi)$ functions about a displaced center presented thoroughly

in (6) makes use of a relatively simple and close formula for the transformation of the multipole moments of characteristic radial dependence $R^{-(L+1)}Y_L^M(\theta, \phi)$ for a parallel shift of the reference system along the z axis

$$\frac{Y_L^M(\theta, \phi)}{R^{L+1}} = \sum_l (-1)^{l+m}(2L + 1)$$

$$\left[\frac{(2l + 2L + 1)!}{(2L + 1)!(2l + 1)!}\right]^{1/2} \qquad [1]$$

$$\begin{pmatrix} l & L & l + L \\ -m & M & m - M \end{pmatrix} \frac{r^l}{a^{l+L+1}} Y_l^m(\vartheta, \varphi),$$

where the R, θ, ϕ coordinates and L, M indices refer to the initial coordinate system centered at the ligand and r, ϑ, φ and l, m to the system shifted along the $Z = z$ axis by a (hence $\theta = \vartheta$ and $M = m$); the factor within the round parentheses is a 3-j symbol.

In the present paper the contribution of only the three basic moments ($L = 0, 1, 2$), monopole, dipole, and quadrupole, respectively, is considered. A formal extension for the higher multipoles is obvious. Thus, the pure multipole potentials become transformed as follows:

$$\frac{Ze}{R} = \left(\frac{4\pi}{5}\right)^{1/2} Ze \frac{r^2}{a^3} Y_2^0(\vartheta, \varphi)$$

$$+ \left(\frac{4\pi}{9}\right)^{1/2} Ze \frac{r^4}{a^5} Y_4^0(\vartheta, \varphi)$$

$$+ \left(\frac{4\pi}{13}\right)^{1/2} Ze \frac{r^6}{a^7} Y_6^0(\vartheta, \varphi) \qquad [2]$$

$$\frac{M_1^0 Y_1^0(\theta, \phi)}{R^2} = -3\left(\frac{3}{5}\right)^{1/2} M_1^0 \frac{r^2}{a^4} Y_2^0(\vartheta, \varphi)$$

$$- 5\left(\frac{1}{3}\right)^{1/2} M_1^0 \frac{r^4}{a^6} Y_4^0(\vartheta, \varphi)$$

$$- 7\left(\frac{3}{13}\right)^{1/2} M_1^0 \frac{r^6}{a^8} Y_6^0(\vartheta, \varphi) \qquad [3]$$

$$\frac{M_1^{\pm1} Y_1^{\pm1}(\theta, \phi)}{R^2} = 3\left(\frac{1}{5}\right)^{1/2} M_1^{\pm1} \frac{r^2}{a^4} Y_2^{\pm1}(\vartheta, \varphi)$$

$$+ \left(\frac{10}{3}\right)^{1/2} M_1^{\pm1} \frac{r^4}{a^6} Y_4^{\pm1}(\vartheta, \varphi)$$

$$+ 3\left(\frac{13}{7}\right)^{1/2} M_1^{\pm1} \frac{r^6}{a^8} Y_6^{\pm1}(\vartheta, \varphi) \qquad [4]$$

$$\frac{M_2^0 Y_2^0(\theta, \phi)}{R^3} = 6 M_2^0 \frac{r^2}{a^5} Y_2^0(\vartheta, \varphi)$$

$$+ 5(5)^{1/2} M_2^0 \frac{r^4}{a^7} Y_4^0(\vartheta, \varphi)$$

$$+ 28\left(\frac{5}{13}\right)^{1/2} M_2^0 \frac{r^6}{a^9} Y_6^0(\vartheta, \varphi) \qquad [5]$$

$$\frac{M_2^{\pm1} Y_2^{\pm1}(\theta, \phi)}{R^3} = -4 M_2^{\pm1} \frac{r^2}{a^5} Y_2^{\pm1}(\vartheta, \varphi)$$

$$- 10\left(\frac{2}{3}\right)^{1/2} M_2^{\pm1} \frac{r^4}{a^7} Y_4^{\pm1}(\vartheta, \varphi)$$

$$- 8\left(\frac{35}{13}\right)^{1/2} M_2^{\pm1} \frac{r^6}{a^9} Y_6^{\pm1}(\vartheta, \varphi) \qquad [6]$$

$$\frac{M_2^{\pm2} Y_2^{\pm2}(\theta, \phi)}{R^3} = M_2^{\pm2} \frac{r^2}{a^5} Y_2^{\pm2}(\vartheta, \varphi)$$

$$+ 5\left(\frac{1}{3}\right)^{1/2} M_2^{\pm2} \frac{r^4}{a^7} Y_4^{\pm2}(\vartheta, \varphi)$$

$$+ 5\left(\frac{14}{13}\right)^{1/2} M_2^{\pm2} \frac{r^6}{a^9} Y_6^{\pm2}(\vartheta, \varphi). \qquad [7]$$

In the expansions given above only the components which are effective from the crystal-field parameterization point of view, i.e., those of $l = 2, 4$ and 6, are shown. Ze denotes the point charge of the ligand and $M_L^{\pm M}$ the corresponding components of its dipole and quadrupole moments.

Equation [2] constitutes the essence of the point-charge model. The contributions of the higher multipole moments (Eq. [3]–[7]) decay with higher powers of a, e.g., by 1 for dipole, by 2 for quadrupole, etc. For $L + M$ odd, the expansion coefficients are negative, for even, they are positive. For fixed L, their absolute values are largest for the axial components and decrease regularly when $|M|$ rises. The radial distribution (within the shifted system) of a component of the angular part $Y_l^m(\vartheta, \varphi)$ is simply r^l/a^{l+L+1}.

2. Translational Transformation of the Screened Multipole Moment

The method of the translational transformation of $f(R) Y_L^M(\theta, \phi)$ functions for other than the multipolar radial dependence (Eq. [1]), e.g., the screened multipole moments, is arranged in the three following steps:

(i) factorizing the function $f(R)Y_L^M(\theta, \phi)$ according to the scheme

$$f(R)Y_L^M(\theta, \phi) = \left(\sum_K a_K R^K\right) R^{-(L+1)} Y_L^M(\theta, \phi), \qquad [8]$$

Equation [18] can be solved by expansion of the $\mathbb{R}(R)$ function into power series of R. However, considering the point $\mathbf{R} = 0$ to be a singular one (although regular) the expansion begins with a certain $K \neq 0$ exponent (12)

$$\mathbb{R}(R) = c_0 R^K + c_1 R^{K+1} + c_2 R^{K+2} + \cdots. \qquad [19]$$

Let's start from the solution for $\lambda = 0$ (an unscreened system), in other words, from the well known solution of the Laplace equation. Then, the so-called indication equation involving the coefficients at the terms of the lowest exponent, i.e., K in this case, has the form

$$c_0 R^K [K(K - 1) + 2K - L(L + 1)] = 0 \qquad [20]$$

and is fulfilled either for $K = L$ or $K = -(L + 1)$. Only the second solution has physical meaning; i.e., it decays with the distance naturally. As it results from all the remaining equations for coefficients at succeeding powers of R all $c_n = 0$ if $n \neq 0$. Exceptionally for $L = 0$ the coefficient c_1 could be different from zero, being an arbitrary constant. However, it is well known that this case corresponds to the point-charge potential and $c_1 = 0$ ought to be taken. Hence, the permissible solutions of Eq. [15] for $\lambda = 0$ have the form of components of the multipole moments:

$$U(\mathbf{R}) = c_0 R^{-(L+1)} Y_L^{\pm M}(\theta, \phi). \qquad [21]$$

For $L = 0$, $c_0 = Ze$; for $L \neq 0$, $c_0 = M_L^{\pm M}$.

In the case of the screening, i.e., for $\lambda \neq 0$, the angular part of the solution remains invariable whereas the radial part undergoes an alteration. The indication equation is the same as the previous one (Eq. [20]) and similarly the solution with $K = -(L + 1)$ is physically acceptable.

For $L \neq 0$ only the coefficients $c_\nu(\nu = 0, 2, 4, \ldots)$ of even indices are different from zero. They are defined by the recurring formula

$$c_\nu = \frac{\lambda^2 c_{\nu-2}}{(K + \nu)(K + \nu + 1) - L(L + 1)} \qquad [22]$$

which after substituting the value $K = -(L + 1)$ takes the form

$$c_\nu = \frac{\lambda^2 c_{\nu-2}}{-2\nu L + \nu^2 - \nu}. \qquad [23]$$

On the other hand, all odd coefficients starting from c_1 vanish.

A particular situation takes place for $L = 0$, i.e., for the screened point-charge potential. Then, the coefficient c_1 does not have to be equal to zero. For $K = -1$ the factor at c_1 in the equivalent of the indication equation is equal

to zero and in consequence all the odd coefficients are related also with Eq. [23]. Since the solution for the screened monopole potential, $(Ze/R) \exp(-\lambda R)$, is known, the constant c_1 is equal to $-\lambda Ze$. Using Eqs. [19] and [23] the following radial functions $\mathbb{R}_L(R)$ of the screened multipoles have been obtained:

$$L = 0, \quad \mathbb{R}_0(R) = \frac{Ze}{R}\left(1 - \lambda R + \frac{1}{2}\lambda^2 R^2 - \frac{1}{6}\lambda^3 R^3 + \ldots\right)$$

$$= \frac{Ze}{R}\exp(-\lambda R) \qquad [24]$$

$$L = 1, \quad \mathbb{R}_1^{\pm M}(R) = \frac{M_1^{\pm M}}{R^2}\left(1 - \frac{1}{2}\lambda^2 R^2 - \frac{1}{8}\lambda^4 R^4 - \frac{1}{144}\lambda^6 R^6\right.$$

$$\left. - \frac{1}{144\cdot 40}\lambda^8 R^8 - \ldots\right) \qquad [25]$$

$$L = 2, \quad \mathbb{R}_2^{\pm M}(R) = \frac{M_2^{\pm M}}{R^3}\left(1 - \frac{1}{6}\lambda^2 R^2 + \frac{1}{24}\lambda^4 R^4\right.$$

$$\left. + \frac{1}{144}\lambda^6 R^6 + \frac{1}{144\cdot 24}\lambda^8 R^8 + \ldots\right). \qquad [26]$$

Only in the case of monopole is the modification factor (in parentheses of Eq. [24]) a fully alternate series. In the remaining cases, all terms, starting from a certain degree, are either negative (for L odd) or positive (for L even). The screened monopole potential decays exponentially with R. The radial dependences for the screened higher multipole potentials are not so simple, especially for larger λ when the absolute value of the modification factor may exceed 1. It is understood that the response of the system consisting in activation of local charge density of conduction electrons (through the Poisson equation) is characterized by a different radial dependence than that for the perturbing potential. The series form of the solution obtained is convenient from the point of view of the translational transformation method applied.

RESULTS

Applying the nonintegral expansion method to the series expansions of the screened multipole potentials (Eqs. [17] and [24]–[26]) gives directly the effective components of the crystal-field potential at the central atom site. The screening effect for $\lambda a = 1, 2$, and 3 is quantitatively estimated. To this end a sufficient accuracy is achieved for expansions (Eq. [24]–[26]) up to twelfth, sixth, and eighth degree with respect to λR for monopole, dipole, and quadrupole, respectively. It may be checked up directly.

Here is a good place to specify certain restrictions concerning r, i.e., the distance measured from the displaced

center (the central atom). From the point of view of the crystal-field effect when we are interested in the influence of a ligand potential on the internal electrons of the central atom, an assumption $r < a/2$ seems to be reasonable. Detailed calculations (see below) show that the radial distribution of the screened multipole potentials about a displaced center has the form $r^l/a^{l+L+1}[1 - \sigma(\lambda, a, r)]$ and the screening factor $\sigma(\lambda, a, r)$ within the whole range $0 < r < a/2$ varies slightly with r, being determined by a rather.

The intrinsic crystal-field parameters are calculated by means of averaging the above radial parts of the potential over the radial distribution of unpaired electrons of the central atom. The same averaging of the $\sigma(\lambda, a, r)$ factor itself leads to the proper value of the $\sigma_{nl}(\lambda, a)$ factor for the specified unpaired electrons (nl).

To compare the screening effect the screening factor has been calculated for a representative distance $r = a/3$. The detailed results are given below. Only these terms in the $\sigma(\lambda, a, r)$ factors which are >0.01 for the limitations assumed ($\lambda a \leq 3$, $r = a/3$) are specified. Within the round parentheses only the important components of the homogeneous polynomials of succeeding degrees with respect to ar are shown.

$$\frac{Ze}{R}\sum_{n=0}^{12}\frac{(-1)^n}{n!}(\lambda R)^n \approx \left(\frac{4\pi}{5}\right)^{1/2}Ze\frac{r^2}{a^3}\left\{1 - \left[\left(\frac{\lambda^2a^2}{6} - \frac{\lambda^2r^2}{14}\right)\right.\right.$$

$$+ \left(-\frac{\lambda^4a^4}{24} + \frac{\lambda^4a^2r^2}{84}\right) + \left(\frac{\lambda^5a^5}{45}\right)$$

$$+ \left(-\frac{\lambda^6a^6}{144} - \frac{\lambda^6a^4r^2}{336}\right) + \left(\frac{\lambda^7a^7}{630} + \frac{\lambda^7a^5r^2}{630}\right) + \left(-\frac{\lambda^8a^8}{3456}\right.$$

$$- \frac{\lambda^8a^6r^2}{2016}\right) + \left(\frac{\lambda^9a^9}{22{,}675} + \frac{\lambda^9a^7r^2}{8820} + \frac{\lambda^9a^5r^4}{22{,}675}\right)$$

$$+ \left(-\frac{\lambda^{10}a^{10}}{172{,}800} - \frac{\lambda^{10}a^8r^2}{48{,}384}\right) + \left(\frac{\lambda^{11}a^{11}}{1{,}496{,}880} + \frac{\lambda^{11}a^9r^2}{317{,}520}\right)$$

$$+ \left(-\frac{\lambda^{12}a^{12}}{14{,}515{,}200} - \frac{\lambda^{12}a^{10}r^2}{2{,}419{,}200}\right)\left]\right\}Y_2^0(\vartheta,\varphi)$$

$$+ \left(\frac{4\pi}{9}\right)^{1/2}Ze\frac{r^4}{a^5}\left\{1 - \left[\left(\frac{\lambda^2a^2}{14} - \frac{\lambda^2r^2}{22}\right) + \left(-\frac{\lambda^4a^4}{280}\right.\right.\right.$$

$$+ \frac{\lambda^4a^2r^2}{308}\right) + \left(\frac{\lambda^6a^6}{5040} - \frac{\lambda^6a^4r^2}{6160}\right)$$

$$+ \left(-\frac{\lambda^8a^8}{40{,}320}\right) + \left(\frac{\lambda^9a^9}{99{,}225}\right) + \left(-\frac{\lambda^{10}a^{10}}{403{,}200}\right)$$

$$+ \left(\frac{\lambda^{11}a^{11}}{2{,}182{,}950}\right) + \left(-\frac{\lambda^{12}a^{12}}{14{,}515{,}200}\right)\left]\right\}Y_4^0(\vartheta,\varphi)$$

$$+ \left(\frac{4\pi}{13}\right)^{1/2}Ze\frac{r^6}{a^7}\left(1 - \left[\left(\frac{\lambda^2a^2}{22} - \frac{\lambda^2r^2}{30}\right) + \left(-\frac{\lambda^4a^4}{792}\right.\right.\right.$$

$$+ \frac{\lambda^4a^2r^2}{660}\right) + \left(\frac{\lambda^6a^6}{33{,}264}\right)\left]\right]\right\}Y_6^0(\vartheta,\varphi)$$

$$\frac{M_1^0 Y_1^0(\theta,\phi)}{R^2}\left(1 - \frac{1}{2}\lambda^2R^2 - \frac{1}{8}\lambda^4R^4 - \frac{1}{144}\lambda^6R^6\right)$$

$$\approx -3\left(\frac{3}{5}\right)^{1/2}M_1^0\frac{r^2}{a^4}\left\{1 - \left[\left(\frac{\lambda^2a^2}{18} - \frac{\lambda^2r^2}{14}\right) + \left(\frac{\lambda^4a^4}{72}\right.\right.\right.$$

$$+ \frac{\lambda^4a^2r^2}{252}\right) + \left(\frac{\lambda^6a^6}{144} + \frac{\lambda^6a^4r^2}{1008}\right)\left]\right]\right\}Y_2^0(\vartheta,\varphi)$$

$$- 5\left(\frac{1}{3}\right)^{1/2}M_1^0\frac{r^4}{a^6}\left\{1 - \left[\left(\frac{3\lambda^2a^2}{70} - \frac{\lambda^2r^2}{22}\right) + \left(-\frac{\lambda^4a^4}{1400}\right.\right.\right.$$

$$+ \frac{3\lambda^4a^2r^2}{1540}\right) + \left(-\frac{\lambda^6a^6}{25{,}200}\right)\left]\right]\right\}Y_4^0(\vartheta,\varphi)$$

$$- 7\left(\frac{3}{13}\right)^{1/2}M_1^0\frac{r^6}{a^8}\left\{1 - \left[\left(\frac{5\lambda^2a^2}{154} - \frac{\lambda^2r^2}{30}\right)\right.\right.$$

$$+ \left(-\frac{\lambda^4a^4}{1848}\right)\left]\right]\right\}Y_6^0(\vartheta,\varphi)$$

$$\frac{M_1^{+1}Y_1^{\pm1}(\theta,\phi)}{R^2}\left(1 - \frac{1}{2}\lambda^2r^2 - \frac{1}{8}\lambda^4R^4 - \frac{1}{144}\lambda^6R^6\right)$$

$$\approx 3\left(\frac{1}{5}\right)^{1/2}M_1^{\pm1}\frac{r^2}{a^4}\left\{1 - \left[\left(\frac{\lambda^2a^2}{6} - \frac{\lambda^2r^2}{14}\right) + \left(-\frac{\lambda^4a^4}{24}\right.\right.\right.$$

$$+ \frac{\lambda^4a^2r^2}{84}\right) + \left(-\frac{\lambda^6a^6}{144} - \frac{\lambda^6a^4r^2}{336}\right)\left]\right]\right\}Y_2^{\pm1}(\vartheta,\varphi)$$

$$+ \left(\frac{10}{3}\right)^{1/2}M_1^{\pm1}\frac{r^4}{a^6}\left\{1 - \left[\left(\frac{\lambda^2a^2}{14} - \frac{\lambda^2r^2}{22}\right) + \left(-\frac{\lambda^4a^4}{280}\right.\right.\right.$$

$$+ \frac{\lambda^4a^2r^2}{308}\right) + \left(\frac{\lambda^6a^6}{5040}\right)\left]\right]\right\}Y_4^{\pm1}(\vartheta,\varphi)$$

$$+ 3\left(\frac{13}{7}\right)^{1/2}M_1^{\pm1}\frac{r^6}{a^8}\left\{1 - \left[\left(\frac{\lambda^2a^2}{22} - \frac{\lambda^2r^2}{30}\right) + \left(-\frac{\lambda^4a^4}{792}\right.\right.\right.$$

$$+ \frac{\lambda^4a^2r^2}{660}\right) + \left(\frac{\lambda^6a^6}{33{,}264}\right)\left]\right]\right\}Y_6^{\pm1}(\vartheta,\varphi)$$

$$\frac{M_2^0 Y_2^0(\theta,\phi)}{R^3}\left(1 - \frac{1}{6}\lambda^2R^2 + \frac{1}{24}\lambda^4R^4 + \frac{1}{144}\lambda^6R^6 + \frac{1}{3456}\lambda^8R^8\right)$$

$$\approx 6M_2^0\frac{r^2}{a^5}\left\{1 - \left[\left(\frac{\lambda^2a^2}{18} - \frac{\lambda^2r^2}{14}\right) + \left(-\frac{\lambda^4a^4}{216} + \frac{\lambda^4a^2r^2}{252}\right)\right.\right.$$

$$+ \left(-\frac{\lambda^6 a^6}{432} - \frac{\lambda^6 a^4 r^2}{3024} \right) + \left(-\frac{\lambda^8 a^8}{3456} \right) \Big] \Big\} Y_2^0(\vartheta, \varphi)$$

$$+ 5(5)^{1/2} M_2^0 \frac{r^4}{a^7} \left\{ 1 - \left[\left(\frac{5\lambda^2 a^2}{126} - \frac{\lambda^2 r^2}{22} \right) + \left(-\frac{13\lambda^4 a^4}{12,600} \right. \right. \right.$$

$$+ \frac{5\lambda^4 a^2 r^2}{2772} \right) + \left(\frac{\lambda^6 a^6}{25,200} \right) \Big] \Big\} Y_4^0(\vartheta, \varphi)$$

$$+ 28 \left(\frac{5}{13} \right)^{1/2} M_2^0 \frac{r^6}{a^9} \left\{ 1 - \left[\left(\frac{\lambda^2 a^2}{33} - \frac{\lambda^2 r^2}{30} \right) \right. \right.$$

$$+ \left(-\frac{\lambda^4 a^4}{1848} \right) \Big] \Big\} Y_6^0(\vartheta, \varphi)$$

$$\frac{M_2^{\pm 1} Y_2^{\pm 1}(\theta, \phi)}{R^3} \left(1 - \frac{1}{6} \lambda^2 R^2 + \frac{1}{24} \lambda^4 R^4 + \frac{1}{144} \lambda^6 R^6 \right.$$

$$+ \frac{1}{3456} \lambda^8 R^8 \right)$$

$$\approx -4 M_2^{\pm 1} \frac{r^2}{a^5} \left\{ 1 - \left[\left(\frac{\lambda^2 a^2}{12} - \frac{\lambda^2 r^2}{14} \right) + \left(\frac{\lambda^4 a^2 r^2}{168} \right) \right. \right.$$

$$+ \left(\frac{\lambda^6 a^6}{288} \right) + \left(\frac{\lambda^8 a^8}{3456} \right) \Big] \Big\} Y_2^{\pm 1}(\vartheta, \varphi)$$

$$- 10 \left(\frac{2}{3} \right)^{1/2} M_2^{\pm 1} \frac{r^4}{a^7} \left\{ 1 - \left[\left(\frac{\lambda^2 a^2}{21} - \frac{\lambda^2 r^2}{22} \right) \right. \right.$$

$$+ \left(-\frac{\lambda^4 a^4}{840} + \frac{\lambda^4 a^2 r^2}{462} \right) \Big] \Big\} Y_4^{\pm 1}(\vartheta, \varphi)$$

$$- 8 \left(\frac{35}{13} \right)^{1/2} M_2^{\pm 1} \frac{r^6}{a^9} \left\{ 1 - \left[\left(\frac{3\lambda^2 a^2}{88} - \frac{\lambda^2 r^2}{30} \right) \right. \right.$$

$$+ \left(-\frac{\lambda^4 a^4}{1584} + \frac{\lambda^4 a^2 r^2}{880} \right) \Big] \Big\} Y_6^{\pm 1}(\vartheta, \varphi)$$

$$\frac{M_2^{\pm 2} Y_2^{\pm 2}(\theta, \phi)}{R^3} \left(1 - \frac{1}{6} \lambda^2 R^2 + \frac{1}{24} \lambda^4 R^4 + \frac{1}{144} \lambda^6 R^6 \right.$$

$$+ \frac{1}{3456} \lambda^8 R^8 \right)$$

$$\approx M_2^{\pm 2} \frac{r^2}{a^5} \left\{ 1 - \left[\left(\frac{\lambda^2 a^2}{6} - \frac{\lambda^2 r^2}{14} \right) + \left(-\frac{\lambda^4 a^4}{24} + \frac{\lambda^4 a^2 r^2}{84} \right) \right. \right.$$

$$+ \left(-\frac{\lambda^6 a^6}{144} - \frac{\lambda^6 a^4 r^2}{336} \right) + \left(-\frac{\lambda^8 a^8}{3456} \right) \Big] \Big\} Y_2^{\pm 2}(\vartheta, \varphi)$$

$$+ 5 \left(\frac{1}{3} \right)^{1/2} M_2^{\pm 2} \frac{r^4}{a^7} \left\{ 1 - \left[\left(\frac{\lambda^2 a^2}{14} - \frac{\lambda^2 r^2}{22} \right) + \left(-\frac{\lambda^4 a^4}{280} \right. \right. \right.$$

$$+ \frac{\lambda^4 a^2 r^2}{308} \right) + \left(\frac{\lambda^6 a^6}{5040} \right) \Big] \Big\} Y_4^{\pm 2}(\vartheta, \varphi)$$

$$+ 5 \left(\frac{14}{13} \right)^{1/2} M_2^{\pm 2} \frac{r^6}{a^9} \left\{ 1 - \left[\left(\frac{\lambda^2 a^2}{22} - \frac{\lambda^2 r^2}{30} \right) + \left(-\frac{\lambda^4 a^4}{792} \right. \right. \right.$$

$$+ \frac{\lambda^4 a^2 r^2}{660} \right) \Big] \Big\} Y_6^{\pm 2}(\vartheta, \varphi)$$

The screening factors $\sigma(\lambda, a, r)$, i.e., the expressions given in the square parentheses of the above formulas, calculated for $\lambda a = 1$, 2, and 3 and $r = a/3$, are compiled in Table 1.

DISCUSSION

The results presented in Table 1 are instructive. Taking into account a high efficiency of free conduction electrons in suppression of the spherically symmetric part of the potential (Y_0^0), one might expect that the higher components forming the crystal-field potential are also seriously reduced. In handbooks we can find a statement that an external perturbation of large wavelength (in its Fourier picture) is almost entirely screened by flow of movable electrons (10), in other words, for $\mathbf{q} \to 0$ the dielectric constant $\varepsilon \to \infty$.

In the light of the given estimation it turns out that the screening efficiency of the ligand field components ($l = 2$, 4, 6) goes down when l rises. The screening factor σ, for $\lambda a \leq 3$, does not exceed 0.5 for $l = 4$ and reaches 0.3 for $l = 6$. Within the considered range of λ the most interesting situation takes place for the second order components. Their factor σ for the potential generated by the point charge gains 0.6 (for $\lambda a = 3$) indeed, but the contributions generated by the dipole and quadrupole moments of the ligand are several times enhanced.

Even taking into account a typical hierarchy of the contributions, i.e., a decay of the role of higher ligand multipoles, the observed effect may thoroughly modify the second-order crystal-field parameters. The amplification of the contributions generated by Y_L^M components of $L + M$ odd alters the sign of the bare unscreened contributions whereas for $L + M$ even the sign is preserved. The resultant parameter may be different depending on the magnitude and sign of Ze charge and $M_L^{\pm M}$ components. This possibility of algebraic summation of the contributions originating from the point charge potential and enhanced (regarding their absolute values) contributions originating from the dipole and quadrupole (and also higher) moments may elucidate several unaccountable and mysterious divergences regarding the second-order parameters met during interpretation of crystal-field splitting schemes.

TABLE 1
Ligand-Field Screening Factor σ for the Monopole, Dipole, and Quadrupole Components of the Ligand Potential According to the Thomas–Fermi Model

Intrinsic component of the ligand field potential	Generating potential					
	Y_0^0	Y_1^0	$Y_1^{\pm1}$	Y_2^0	$Y_2^{\pm1}$	$Y_2^{\pm2}$
Y_2^0	0.13	0.07		0.04		
	0.23	0.87		−0.10		
	0.61	6.73		−3.52		
$Y_2^{\pm1}$			0.11		0.08	
			−0.48		0.61	
			−7.14		5.16	
$Y_2^{\pm2}$						0.11
						−0.55
						−9.04
Y_4^0	0.06	0.04		0.03		
	0.23	0.14		0.13		
	0.40	0.27		0.27		
$Y_4^{\pm1}$			0.06		0.04	
			0.23		0.16	
			0.48		0.31	
$Y_4^{\pm2}$						0.06
						0.23
						0.48
Y_6^0	0.04	0.03		0.03		
	0.15	0.11		0.10		
	0.30	0.22		0.20		
$Y_6^{\pm1}$			0.04		0.03	
			0.15		0.11	
			0.31		0.23	
$Y_6^{\pm2}$						0.04
						0.15
						0.29

Note. Comparative values for $\lambda a = 1, 2, 3$, $r = a/3$, where λ is the Thomas–Fermi wave vector, a is the central atom–ligand distance, and r is the distance from the central atom. In each cell the σ value in the first row is for $\lambda a = 1$, in the second row for $\lambda a = 2$, and in the third row for $\lambda a = 3$, respectively.

Undoubtedly, the effect of strong amplification of the contributions from dipole and quadrupole moments (as well as higher ones, ignored here) is intriguing. The effect results directly from solutions (Eq. [24]–[26]). Any bare local potential $V(\mathbf{R}) = U(\mathbf{R})\varepsilon(\mathbf{R})$, i.e., that before self-consistence, independently on its radial dependence (but subject to a slow-variability) activates a charge proportional to the density of states at the Fermi surface. For a large $\lambda = -4\pi e^2 N(F_\mathrm{F})$ the resultant self-consistent potential being a solution of the Poisson's equation overcomes completely the inducing bare potential.

It should be emphasized that the presented results have a pretty universal meaning. Considering the weak dependence of $\sigma(\lambda, a, r)$ on r/a the screening factor is determined mainly by the λa dimensionless parameter only, i.e., by the screening radius expressed in terms of the lattice parameter.

In conclusion, all limitations of the present approach resulting from the assumptions introduced should be restated:

—Only the electrostatic contributions to the crystal-field parameters (13) are considered. Nevertheless, joint contributions of the point charge and the dipolar and quadrupolar polarizations are an important part of the whole effect (13, 14).

—The presented approach deals with a central atom–ligand static system and neglects the lattice vibrations as well as the plasma oscillations of the free-electron gas. In fact, the electrons are involved in an organized collective vibration motion of characteristic angular frequency $\omega_\mathrm{p} = [3e^2/(mr_\mathrm{s}^3)]^{1/2}$. The screening effect calculated in this dynamical approach is less effective than that for the free electrons (15, 16). Therefore we reflect that the screening results presented in this paper are rather overestimated.

—One should remember the simplifications of the Thomas–Fermi model itself and particularly the requirement of slow-variability of the perturbing potential. A potential $U(\mathbf{R})$ may be recognized as slowly variable if for an electron at point $\mathbf{R}$ its energy can be described in the form $E(\mathbf{k}) = \hbar^2 k^2/(2m) - eU(\mathbf{R})$ and this is reasonable if the potential $U(\mathbf{R})$ changes slightly only along distances comparable with a typical wave packet size of the electron which amounts $\sim 1/k_\mathrm{F}$, in other words for distances of order a. The Thomas–Fermi approach is a long-wave ($\mathbf{q} \to 0$) approximation valid for potentials of the long-wave Fourier spectrum. The Fourier transform of the point charge potential Ze/R has the form $V(\mathbf{q}) = 4\pi e/q^2$ from which it is seen that the short-wave components are not very important. Unfortunately, for the higher multipoles their role rises and they have a negative influence upon the adequacy of the model.

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