

## Collapse of $f$ -electron wave function of $Tl^{3+}$ ion in a crystal field

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The radial wave functions of  $Tl^{3+}$  ion doped into introduced KCl crystal lattice have been calculated. The calculations were carried out by a Hartree-Fock-Slater method in the field of the "frozen" frame, i.e. without self-consistency with the wave functions of internal electrons. A new model taking into account the crystal lattice field influence has been proposed. In this model, the exchange interaction is taken into account in addition to electrostatic interaction with the lattice ions. The exchange interaction is taken into account using the Slater correction. In the approach of the present model, the  $5f$ -electron wave function collapse of  $Tl^{3+}$  ion is observed. The result obtained testifies to assumption that one of  $Tl^{3+}$  ion absorption bands is attributed to  $5d^{10} \leftrightarrow 5d^9 5f$  transition.

Рассчитаны радиальные волновые функции иона  $Tl^{3+}$ , внедренного в кристаллическую решетку KCl. Расчет проводился методом Хартри-Фока-Слэтера в поле "замороженного" остова, т.е. без самосогласования с волновыми функциями внутренних электронов. Для учета влияния поля кристаллической решетки была предложена новая модель, в которой кроме электростатического взаимодействия с ионами решетки учтено также обменное взаимодействие. Обменное взаимодействие учтено с помощью поправки Слэтера. В приближении данной модели наблюдается коллапс волновой функции  $5f$  электрона. Полученный результат говорит в пользу сопоставления одной из полос поглощения активаторного иона  $Tl^{3+}$  с переходом  $5d^{10} \leftrightarrow 5d^9 5f$ .

The  $f$ -electron collapse possibility in excited ( $5d^9 6s^2 5f$ )  $Tl^+$  ion introduced into an alkali halide crystal matrix [1–3] as a result of the nearest environment influence on its electronic shell was predicted in [4, 5]. Such prediction correlates with results of experimental research of absorption and luminescence spectra of electrolyte solutions containing others mercury-like ions as an activator [6–10].

The wave functions of a free ion are often used at theoretical estimations of the luminescence centers. Such an approach is based on the prediction of small influence of the activator ion environment on its wave functions. The direct calculations of radial wave functions of  $Tl^+$  ion ( $5d^{10} 6s^2$ ) introduced into KCl, KBr, and KI crystals confirmed this prediction [11]. However, in spite of the fact that the introduction of a  $Tl^+$  ion into KCl crystal is accompanied by an insignificant change of  $d$ - and  $s$ -electron

radial wave functions [11], the environment influence on the  $f$ -electron radial wave function sometimes appears to be significant. This may be caused by a possibility of  $f$ -electron radial wave function collapse. To simplify the calculations, the  $5f$ -electron radial wave function of  $Tl^{3+}$  ion (instead of  $Tl^+$  one) for  $5d^9 5f$  electron configuration is calculated in this work. At the calculations, the influence of KCl crystal lattice field has been taken into account. The technique of taking into account the crystal lattice field influence has been changed significantly in comparison with [11].

The  $5f$ -electron wave function of  $Tl^{3+}$  ion with  $5d^9 5f$  electron configuration is calculated by Hartree-Fock-Slater method (HFS) in the field of "frozen" internal electrons. For this purpose, the system of differential equations was solved which, in atomic system of units looks like

$$Z' = P^2, \quad (1)$$

$$W' = (\varepsilon + l(l+1)/r^2 + 2(U_{ef} + U_{av}))P, \quad (2)$$

$$P' = W, \quad (3)$$

where  $Z$  is the electron shell effective charge intensity;  $P$ , the  $5f$ -electron radial wave function;  $\varepsilon$ , double energy eigenvalue;  $l$ , the orbital quantum number ( $l = 3$  for  $f$ -electron);  $U_{ef}$ , effective potential created by a nucleus and others electrons of the  $\text{Tl}^{3+}$  ion based on the data from [12];  $U_{av}$  is sphere-averaged potential of the lattice,  $U_{Lat}(x,y,z)$ . The functions included in the system of equations (1–3) have to satisfy the following boundary conditions:  $Z(0) = 0$ ,  $Z(\infty) = 1$ ,  $P(0) = P(\infty) = 0$ . The radial wave function of  $f$ -electron should have one knot within the range  $0 < r < \infty$ . The integration of system (1–3) was carried out from large values of  $r$  ( $\sim 30$ ).

Let  $U_{ef}$  and  $U_{av}$  potentials presented in (2) be considered in more detail. As noted above, the introduction of thallium ion into a crystal lattice is accompanied by insignificant changes in radial wave functions of  $d$ - and  $s$ -electrons. These changes can be neglected when passing to various configurations of external electron shells of thallium ion, too [11, 14, 17]. The weak dependence of radial wave functions of  $d$ - and  $s$ -electrons on the external electron shell configuration and environment of the ion allows us to simplify the calculations. In contrast to the method described in [14], the  $f$ -electron wave function was calculated in the field of "frozen"  $d$ -,  $s$ -and others inner electrons. In that case, the potential  $U_{ef}$  can be described as

$$U_{ef} = \int_r^\infty \left( \frac{\int_0^r \sum_i P_i^2(r) dr}{r^2} \right) dr - \frac{Z_{\text{Tl}}}{r} - \left( \frac{81 \sum_i P_i^2(r)}{32\pi^2 r^2} \right)^{1/3}, \quad (4)$$

where the first item takes the electrostatic field of "frozen" internal electrons into account, the second one describes the field created by the ion nucleus, and the third one is the Slater simple approximation, which takes into account the  $f$ -electron exchange interaction with others electrons of thallium ion;  $P_i(r)$  is radial wave functions of internal electrons taken from [12];  $r$  is

distance from the ion center;  $Z_{\text{Tl}}$  is the charge of thallium ion nucleus ( $Z_{\text{Tl}} = 81$ ). The case of  $U_{ef}$  potential in the formula (2) corresponds to a free ion. It is necessary to introduce additional potential  $U_{av}$  that would take into account the crystal lattice sphere-averaged field, in order to conduct our calculation for the case of the ion.

A new model taking into account the crystal lattice influence on wave functions of the activator electrons is proposed in this work. In this model, the lattice space is divided into equal cubic cells. The length of each cell edge is equal to the distance between nuclei of the nearest ions,  $d$ . The cells are located in space so that the center of each cell coincides with the nucleus of the appropriate ion. At the first stage, it is necessary to find the potential distribution in each cell using the potential estimation procedure and at second one, to average it over a sphere with the center in the activator ion.

The potential inside each cell can be presented as the sum of three components. The first one is the  $U_m$  potential created by all ions of the lattice except for the ion located inside the suggested cell. The second one is the  $U_s$  potential created inside the cell by the ion located therein. The third component is caused by exchange interaction of the activator ion  $f$ -electron with the electrons of the lattice ions.

Let each component be considered. The potential created at the cell center by all other ions of the lattice is the value known as Moudelung potential taken with appropriate sign for cation and anion. It is necessary to consider the behavior of potential created by all ions of the lattice except for the nearest ones at various points of the appropriate cell (for short, we will further refer to it as to Moudelung potential). To that end, it is necessary to consider the sums similar of those used when calculating the Moudelung constant. However, in this case, the calculations are performed for an arbitrary point within the cell and not for its center.

Let the following introduce designations be introduced:

$$\begin{aligned} n_x &= \text{round}(x/d), \quad n_y = \text{round}(y/d), \\ n_z &= \text{round}(z/d), \quad n = n_x + n_y + n_z, \end{aligned} \quad (5)$$

where  $n_x$  stands for the number of the cell with the point  $(x, 0, 0)$ , counting from the zero cell occupied by the activator ion;  $n_y$

and  $n_z$  numbers have the similar sense. The function  $\text{round}(x/d)$  approximates the number  $x/d$  up to its nearest integer. The coordinate axes are directed along the 4<sup>th</sup> order crystallographic. The coordinate origin is at the center of the cell occupied by the activator ion.

Let us consider the behavior of potential created by all ions of the lattice except for the ion located in this cubic cell. The location of each ion of the lattice can be described by a vector  $\mathbf{a}_{k,l,m}^T = [dk, dl, dm]$ , where  $k, l, m$  are integers. Let us consider a point  $\mathbf{r}'^T = [x', y', z']$  within the suggested cell. The distance between the  $(k, l, m)$  ion and point with coordinates  $(x', y', z')$  is determined by the  $\mathbf{b}_{k,l,m} = \mathbf{a}_{k,l,m} - \mathbf{r}'$  vector. The potential  $U_{k,l,m}(r')$  created at  $\mathbf{r}'$  point by the  $(k, l, m)$  ion in view of its sing is expressed as

$$U_{k,l,m}(x, y, z) = (-1)^{k+l+m} / |\mathbf{b}_{k,l,m}(r')|.$$

The potential  $U_N(x, y, z)$  created by  $N = (2q)^3 - 1$  ions that are contained in a cube with edge length  $2qd$  is calculated as the sum

$$U_N(r') = \sum_{k=-ql}^q \sum_{l=-qm}^q \sum_{m=-q}^q U_{k,l,m}(x,y,z). \quad (6)$$

At summation (6), the point  $k = l = m = 0$  is excluded.

Calculations for various number  $N$  taking into account the lattice ions have shown that it is possible to consider the potential created by all lattice ions except for nearest ones is essentially constant at the cubic cell boundaries. A change in number of ions taken into account changes only the potential absolute value within the cell limits. When taking into account all lattice ions, this value should be equaled to Moudelung potential for the given lattice type. It enables to state that it is possible to present Moudelung potential  $U_m(x, y, z)$  at the points of space filled with the lattice as step function

$$U_m(x,y,z) = U_{m0} \cdot (-1)^n + St/r, \quad (7)$$

where  $r = (x^2 + y^2 + z^2)^{1/2}$  is the distance from the activator ion center and  $n$  depends from  $x, y, z$  (5).

The function

$$St = \exp(-(\ln 2)\exp(-2(r - r_{ion})))$$

is equal to 1 outside of the activator ion and to 0 inside it where rion is the thallium ion radius [11]. It is included into (7) for the following reasons. The Moudelung potential takes account of potentials of all ions of the lattice including that of activator ion  $-1/r$ . However, this potential is included also into  $U_{ef}$  (effective potential of activator ion). In order to not take it into account twice, outside of the cell it is excluded from the Moudelung potential by means of  $St/r$  item.

The second component of effective potential is created by the ion located in the suggested cell. It is necessary to know the electron density distribution of appropriate ion to estimate this component. Distributions of cation  $K^+$  and anion  $Cl^-$  electron density were calculated using the data from [13] and [14], respectively. The designed distributions of cation and anion electron density are presented numerically. To simplify account for those electron density distributions, those approximated by functions of the kind

$$\rho_i(r) = c_i(1 - \exp(-b_i r^2))\exp(-a_i r), \quad (8)$$

where the index  $i$  corresponds either to anion or to cation. In order to calculate the complete effective potential created by the appropriate ion, it is necessary to take into account nucleus potential  $U^n_i(r)$ , too:

$$U^n_i(r) = Z_i/r, \quad (9)$$

where  $Z_i$  is charge of the appropriate ion nucleus. In such case, the complete effective potential  $U^s_i(r)$  created by the ion in a cell which it occupies will be equal to

$$U^s_i(r) = U^n_i(r) + U^e_i(r). \quad (10)$$

The use of  $U^s_i(r)$  potential presented numerically will cause large difficulties in the further work, as sphere-averaging of the lattice potential is necessary. To avoid this problem, we will find the volume-averaged potential created by the appropriate ion in the cell occupied therewith. This average value is possible to find by integrating the  $U^s_i(r)$  potential over the cell volume and dividing the value obtained by the cell volume:

$$\langle U_i \rangle = \int_{-d/2}^{d/2} \int_{-d/2}^{d/2} \int_{-d/2}^{d/2} \frac{U^s_i(x,y,z)dr}{d^3}.$$

Table. Parameters of function (7) and values of averaged potential  $U_i^s$

Ion	$a$	$b$	$c$	$\langle U_i \rangle$ (a. u. s.)
K <sup>+</sup>	1.22946	1655.18114	22.60685	0.6215 ( $\langle U_c \rangle$ )
Cl <sup>-</sup>	0.9	1511.35152	16.56126	-0.0389

It is necessary to find average value  $\langle U \rangle$  of potential  $\langle U_i \rangle$  over the lattice. Since in used approach, the volumes of cells occupied by the anion and cation are identical, then  $\langle U \rangle = (\langle U_a \rangle + \langle U_c \rangle)/2$ .

For KCl lattice the calculated average values of the potential over the lattice volume and over volumes of cells occupied by the anion and cation are presented in Table.

The obtained potential distribution characteristic in the lattice is similar to the behavior of the Moudelung potential distribution, that is, the potential in each cell is constant and is equal  $\langle U_a \rangle$  for an anion-occupied cell and  $\langle U_c \rangle$  for a cation-occupied one. Similarly to the formula describing Moudelung potential, in such case it is possible to write expression for distribution of potential  $U_s(x, y, z)$  over the lattice volume:

$$U_s(x, y, z) = ((\langle U_a \rangle - \langle U_c \rangle)/2) \cdot (-1)^n - \langle U \rangle. \quad (11)$$

A more simple HFS method is applied often when calculating the wave functions instead of a rather difficult Hartree-Fock (HF) method. This method produces results close to those obtained by HF method. In this case, non-local exchange term  $U^{ex}(r_1, r_2)$  is used instead of local potential  $U_L(r)$  in HF equations [15]:

$$U_L(r) = 3(3\rho'(r)/\pi)^{1/3}/2, \quad (12)$$

where  $\rho'(r)$  is electron density:

$$\rho'(r) = \sum_j \varphi_j^*(r) \cdot \varphi_j(r).$$

In this case, the system of HF equations is transformed to a more simple system of equations similar to that of the Hartree equations with the additional term in potential as (12) with negative sign.

In this work, we shall proceed from the assumption that (12) is applicable not only to electrons of  $\text{Ti}^+$  ion, but also to electrons of the lattice ions. Knowing the radial distribution of electron density  $\rho_i(r)$  for cation and anion, let us to find the electron density distribution over the lattice volume. To that end, it is necessary to take into account that the radial distribu-

tion of electron density  $\rho_i(r')$  and non-radial distribution  $\rho'_i(r')$  for a lattice ion corresponds to  $\rho(r') = 4\pi r'^2 \rho'(r')$ , where  $r'$  is counted from the center ( $n_x, n_y, n_z$ ) of suggested ion connected to system of coordinates ( $x, y, z$ ) with the origin at the activator ion nucleus through a relation  $r'^2 = (x - n_x d)^2 + (y - n_y d)^2 + (z - n_z d)^2$ .

Taking into account (4), (9), (10), the expression for electron density distribution over the lattice volume can be presented as

$$\rho(x, y, z) = \frac{(1 - (-1)^n) \cdot \rho_a(x, y, z) + (1 + (-1)^n) \cdot \rho_k(x, y, z)}{2},$$

$$\rho_i(x, y, z) = \rho_{0i} \exp(-a_i r') (1 - \exp(-b_i r'^2)).$$

The complete effective potential of the lattice  $U_{Lat}(x, y, z)$  is equal to the sum of potentials found using (7), (11), and (12):

$$U_{Lat}(x, y, z) = U_m(x, y, z) + U_s(x, y, z) + U_p(x, y, z).$$

The sphere averaging of  $U_{Lat}(x, y, z)$  potential is necessary to calculate the  $\text{Ti}^+$  radial wave functions in approximation of spherical potential:

$$U_{av}(r) = \frac{\int_0^{\pi} \int_0^{2\pi} U_{Lat}(r \sin\theta \cos\varphi, r \sin\theta \sin\varphi, r \cos\theta) \sin\theta d\theta d\varphi}{4\pi}.$$

The calculated 5f-electron radial wave function of  $\text{Ti}^{3+}$  ion in the excited state with the configuration of external electronic shell  $5d^9 5f$  taking place in the KCl lattice field is presented in Fig. 1. The 5f-electron radial wave functions of free univalent thallium ion taken from [14] and trivalent one calculated using the method of "frozen" inner electrons are shown for comparison in this Figure, too.

It is seen that collapse of 5f-electron wave function of  $\text{Ti}^{3+}$  ion introduced into KCl lattice is observed as compared to free  $\text{Ti}^+$  ion. A little shift of the 5f-electron radial wave function toward the nucleus of  $\text{Ti}^{3+}$  ion introduced into KCl lattice as com-

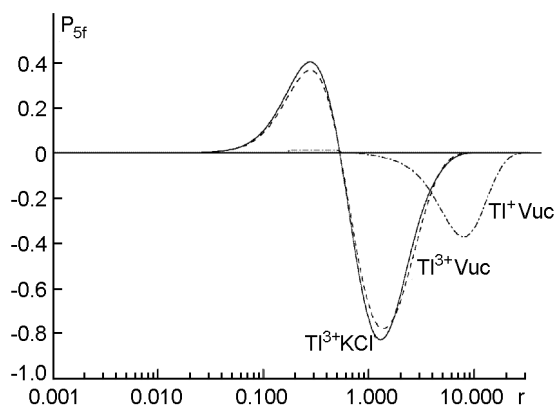


Fig. 1.  $5f$ -electron radial wave functions of  $Ti^{3+}$  ion introduced into KCl lattice (solid), free  $Ti^{3+}$  ion (dash) and free  $Ti^+$  ion (dash-dot).

pared to free  $Ti^{3+}$  ion is observed, too. The result obtained can be interpreted suggesting that one of  $Ti^{3+}$  ion absorption bands is attributed to  $5d^{10} \rightarrow 5d^9 5f$  transition.

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## Колапс хвильової функції $f$ -електрона іона $Ti^{3+}$ у кристалічному полі

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Розраховано радіальні хвильові функції іона  $Ti^+$ , впровадженого у кристалічну ґратку KCl. Розрахунок проводився методом Хартри-Фока-Слетера у полі "замороженого" остова, тобто без самоузгодження з хвильовими функціями внутрішніх електронів. Для урахування впливу поля кристалічної решітки запропоновано нову модель, у якій крім електростатичної взаємодії з іонами решітки враховано також обмінну взаємодію. Обмінна взаємодія врахована за допомогою апроксимації Слетера. У наближенні даної моделі спостерігається колапс хвильової функції  $5f$  електрона. Отриманий результат свідчить на користь співставлення однієї зі смуг поглинання активаторного іона  $Ti^{3+}$  з переходом  $5d^{10} \leftrightarrow 5d^9 5f$ .