Orientation dependence of the energies of *K* x-ray emission lines and relativistic theory of the splitting of core *p* levels of atoms in single crystals and of the angular distribution of the emission

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The shift and splitting of a core hole *p* level in a weak crystal field of trigonal symmetry are analyzed in the relativistic case by perturbation theory. Relativistic angular distributions of the *K*-emission intensity are derived for eigenfunctions which are transformed by irreducible representations of the double groups. The orientational shifts of the *K* x-ray lines in anisotropic crystals are determined by the splitting $\Delta\varepsilon$ of the *p* levels. Determining $\Delta\varepsilon$ experimentally requires knowledge of the angular distribution of the emission of the components of the multiplet. In previous papers, experiments on the orientational shifts and polarization spectra have been interpreted on the basis of the nonrelativistic equations. It is shown that the values found for $\Delta\varepsilon$ from experiments with the help of the relativistic equations may differ by a factor ranging from 4/3 to 2, depending on the spin-orbit splitting. The splitting of the core *p* levels has been found for niobium ions in a lithium metaniobate single crystal. The general results found here can be used to interpret experiments on angular and spin-polarized photoelectron spectroscopy and on electron energy-loss spectroscopy (a study of the orientation dependence of the core absorption edge) of the new, highly anisotropic phases of high T_c superconductors which are structurally related to lithium metaniobate.

1. INTRODUCTION

The energy levels of inner atomic shells in solids are being studied by high-precision experiments in electron and x-ray spectroscopy.[1-3] Analysis of the chemical shifts and splitting of the core levels of atoms in a crystal can provide information about the effective charges and the symmetry of the crystal field.[4,5] The interaction of inner-shell electrons with the weak crystal field is considerably weaker than the interactions within atoms. For this reason, the components of a multiplet which are split in a field are generally not resolved in ordinary x-ray emission spectra or photoelectron spectra. One accordingly observes a superposition of the components of a multiplet, as broadened core lines with an unclear structure. In this case, a quantitative interpretation of experimental results can be carried out, and information on the splitting of atomic levels in a crystal can be found, only by comparing the experimental spectra with theoretical spectra calculated with adjustable parameters.

In principle, a study of polarized x-ray emission spectra[6] would make it possible to obtain additional information on the symmetry of the electronic states of the components of a multiplet. For example, if the spin is ignored, the triply degenerate core *np* level (in the nonrelativistic approximation) splits into components np_x, np_y, and np_z in a field of noncubic symmetry. It follows from the selection rules that the emission for the transitions np_x, np_y, $np_z \to 1s$ will be polarized parallel to the *x*, *y*, and *z* axes, respectively. This polarized emission can be measured for single crystals, so it is possible in principle to completely separate the split components of a multiplet. The components can also be separated by studying[7] the orientation dependence of the parameters of a line in the characteristic x-ray spectrum (the spectral position, magnitude, width, and asymmetry index of the intensity maximum) of atoms in single crystals.

The possibility in principle of separating the components of a multiplet as outlined above prevails only if the spin-orbit splitting is considerably smaller than the crystal splitting. According to Bethe's classification,[8] this case corresponds to the case of intermediate field. Even for the outermost core levels of comparatively light elements, the opposite situation usually prevails[6] (the "weak-field case" in Bethe's classification). Incorporating the spin-orbit interaction in this case leads to a mixing of the functions of the np_x, np_y, and np_z components. For this reason, a study of the linearly polarized emission[6] or of the parameters of a line[7] as a function of the emission direction would not reveal the actual components of a multiplet in the absence of knowledge of the corresponding selection rules for the emission with a given polarization or the angular distribution of these components. Our purpose in the present paper is to examine the last, more general question in the limit of pure *jj* coupling (the relativistic case). The selection rules which we need can easily be extracted from the general equations derived below. We also derive, in the relativistic case, general expressions for the shift and splitting of a core level of an atom in a weak crystal field in the model of point ions. A specific calculation on the splitting of *np* levels is carried out for niobium ions in a lithium metaniobate single crystal.

2. SHIFT AND SPLITTING OF A CORE *p* LEVEL IN A WEAK CRYSTAL FIELD OF TRIGONAL SYMMETRY

The shift and splitting of the core *p* levels of an atom in a single crystal are calculated on the basis of a crystal-field theory.[4] The Hamiltonian of the system is written in the form

$$H=H_0+V, \qquad (1)$$

where H_0 is the Hamiltonian of the free ion, and the operator

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V represents the interaction of this ion with the crystal field set up by the ligands of the complex. The electronic structure of the central ion is taken into consideration. The ligands are assumed to be point sources of an external electrostatic field which perturbs the energy levels of the ion. Since we are interested in the effect of the crystal field on the inner shells of the central ion, which do not overlap with the ligands, the model of point ions should be adequate in this case. In the case of a weak field the interaction V is considerably weaker than the intraatomic interactions. The splitting of the $4p$ level of the niobium ion by the crystal field in a lithium metaniobate single crystal, for example, is $\lesssim 0.1$ eV, while the spin-orbit splitting of the same level is ~ 2 eV (Ref. 9). Perturbation theory can thus be used to determine the splitting of the np level of the ion.

In the $np \to 1s$ x-ray transition, the np shell, which is completely filled in the initial state, has a vacancy in the final state. In a field with a potential V which has a crystal symmetry lower than cubic, the final-state term np^5, which is degenerate in terms of magnetic quantum number, splits. This splitting can be predicted qualitatively by group-theoretical methods. For example, the crystal structure of lithium metaniobate has the trigonal symmetry of the C_{3v} point group (Ref. 10). In the nonrelativistic approximation, a triply degenerate p level in a field of this symmetry splits in two—into a nondegenerate p_z level and a doubly degenerate p_{xy} level—in accordance with the irreducible representations Γ^1 and Γ^3 of the C_{3v} group. We assume that the z axis coincides with the symmetry axis of the crystal. In the relativistic case, the $p_{1/2}$ level does not split according to the Kramers theory, while the $p_{3/2}$ level splits into two doubly degenerate levels, in accordance with the double-valued irreducible representations Γ^1 and Γ^3_{ab} of the double group C'_{3v}.

In the relativistic treatment below, we find the splitting of the $np_{3/2}$ level of an atom in a trigonal crystal field. Instead of the $np^3_{3/2}$ configuration we consider the complementary $np^1_{3/2}$ configuration.

Using perturbation theory for the case of degenerate states, we find a fourth-degree secular equation for the correction ε to the energy level:

$$\|V_{mm'} - \varepsilon\delta_{mm'}\| = 0, \tag{2}$$

where m is the projection of the total angular momentum of the electron; and $m, m' = -3/2, -1/2, 1/2, 3/2$. The matrix element $V_{mm'}$ of the interaction of the central ion with the field of the ligands which are fixed at the points $\mathbf{R}_i(R_i, \theta_i, \varphi_i)$, $i = 1,2,...,N$, is

$$V_{mm'} = \sum_{i=1}^{N} eQ_i \int \frac{\psi^*_{lj\,m}\psi_{ljm'}}{|\mathbf{r}-\mathbf{R}_i|}\, d\tau. \tag{3}$$

Here Q_i is the effective charge of the ligand, N is the number of ligands in the complex, and $e = +1$, since we are dealing with an auxiliary electronic configuration, i.e., a hole. We write the relativistic four-component electron wave function ψ_{ljm} in the form

$$\langle\psi_{ljm}| = \begin{pmatrix} g_{nlj}(r)\,\chi_{ljm}(\theta,\varphi) \\ if_{nlj}(r)\,\chi_{\bar{l}jm}(\theta,\varphi) \end{pmatrix}, \tag{4}$$

where $\chi_{ljm}(\theta, \varphi)$ is a spherical spinor, l and j are respectively the orbital and total angular momenta of the electron, $\bar{l} = 2j - l$, and $g_{nlj}(r)$ and $f_{nlj}(r)$ are respectively the large and small components of the radial electron wave function, which satisfy a system of radial Dirac equations:

$$\begin{cases} \dfrac{dg}{dr} = -\dfrac{\varkappa+1}{r}g + \dfrac{1}{\hbar c}\,[E+mc^2-\tilde{V}(r)]\,f, \\[2ex] \dfrac{df}{dr} = \dfrac{\varkappa-1}{r}f - \dfrac{1}{\hbar c}\,[E-mc^2-\tilde{V}(r)]\,g. \end{cases} \tag{5}$$

Here $\tilde{V}(r)$ is the potential energy of the electron, $\varkappa = (l-j)(2j+1)$, and E is the total energy of the electron, including its rest energy.

Expanding the function $|\mathbf{r} - \mathbf{R}_i|^{-1}$ in (3) in Legendre polynomials, and using the addition theorem for spherical harmonics, we find

$$\frac{1}{|\mathbf{r}-\mathbf{R}_i|} = \sum_k \sum_{q=-k}^{k} \frac{4\pi}{2k+1}\frac{r_<^k}{r_>^{k+1}}\,Y_{kq}(\theta,\varphi)\,Y^*_{kq}(\theta_i,\varphi_i), \tag{6}$$

$$V_{mm'} = \left\langle nljm \left| \frac{1}{|\mathbf{r}-\mathbf{R}_i|} \right| nljm' \right\rangle = \sum_k \mathcal{R}_k(R_i) \sum_q (-1)^q$$

$$\times T^k_{-q}(\theta_i,\varphi_i)\,\langle ljm|\,T^k_q(\theta,\varphi)\,|ljm'\rangle, \tag{7}$$

where

$$T^k_q(\theta,\varphi) = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_{kq}(\theta,\varphi),$$

and the radial integral $\mathcal{R}_k(R_i)$ is

$$\mathcal{R}_k(R_i) = \frac{1}{R_i^{k+1}} \int_0^{R_i} r^{k+2}\,[g^2(r) + f^2(r)]\,dr$$

$$+ R_i^k \int_{R_i}^{\infty} \frac{1}{r^{k-1}}\,[g^2(r) + f^2(r)]\,dr. \tag{8}$$

In the matrix element $\langle ljm|\,T^k_q\,|ljm'\rangle$ in (7), we can separate the dependence on the projections m with the help of the Wigner-Eckart theorem:

$$\langle ljm|\,T^k_q\,|ljm'\rangle = C^{jm}_{jm'kq}(2j+1)^{1/2}\langle lj\|T^k\|lj\rangle, \tag{9}$$

where $C^{jm}_{jm'kq}$ is the Clebsch-Gordan coefficient. The reduced matrix element of the irreducible tensor operator T_k is calculated from

$$\begin{aligned} \langle lj\|T^k\|lj\rangle &= (-1)^{1/2+k-l-j}(2j+1)\langle l\|T^k\|l\rangle W[ljlj;{}^1\!/_2k] \\ &= (-1)^{1/2+k-l-j}(2j+1)\,(2l+1)^{1/2}C^{l0}_{l0k0}W[ljlj;{}^1\!/_2k] \\ &= (2j+1)^{1/2}C^{j1/2}_{j1/2k0}\left(\frac{1+(-1)^k}{2}\right), \end{aligned} \tag{10}$$

where $W[ljlj; \frac{1}{2}k]$ is the Racah coefficient. We finally find the following expression for $V_{mm'}$ (k is even):

$$V_{mm'} = \sum_{i=1}^{N} Q_i \sum_{0\leqslant k\leqslant 2j} \left[\frac{4\pi}{2k+1}\right]^{1/2} (-1)^{m-m'}\,Y_{k\,m-m'}$$

$$\times (\theta_i,\varphi_i)\,C^{j1/2}_{j1/2k0}\,C^{jm}_{jm'km-m'}\,\mathcal{R}_k(R_i). \tag{11}$$

The matrix $\|V_{mm'}\|$ could in general be nondiagonal. Replacing the ψ_{ljm} by the functions φ_{Γ^α}, which are transformed by irreducible representations Γ^1 and Γ^3_{ab} of the group C'_{3v}, we can find the diagonal matrix $\|V_{\Gamma^\alpha\Gamma^\alpha}\|$. Following Ref. 11, we write the functions φ_{Γ^α} for the angular momentum with projections $m = \pm 1/2, \ \pm 3/2$ as follows:

$$\begin{aligned}
\varphi_{\Gamma^1}^{(1)} &= \psi_{lj^1/_2},\\
\varphi_{\Gamma^1}^{(2)} &= (-1)^{l+j+1/2}\psi_{lj-1/2},\\
\varphi^{(1)}_{\Gamma_a^3} &= \frac{1}{2^{1/2}}[\psi_{lj_{3/2}} - i(-1)^{l+j+1/2}\psi_{lj-3/2}],\\
\varphi^{(1)}_{\Gamma_b^3} &= \frac{1}{2^{1/2}}[-i\psi_{lj^3/_2} + (-1)^{l+j+1/2}\psi_{lj-3/2}].
\end{aligned} \tag{12}$$

The superscript specifies functions which are transformed by the same irreducible representation.

The matrix $\|V_{\Gamma^\alpha\Gamma^\alpha}\|$ constructed from functions (12) is diagonal, since the representations Γ^3_a and Γ^3_b are mathematically one-dimensional, and for the two-dimensional representation Γ^1 the functions $\psi_{lj1/2}$ and $\psi_{lj-1/2}$ do not mix. For the diagonal matrix elements V_{Γ^α}, we can use (11) to find the following expressions:

$$\begin{aligned}
V_{\Gamma^1}^{(1)} = V_{\Gamma^1}^{(2)} &= \sum_{i=1}^{N} Q_i[\mathscr{R}_0(R_i)+0{,}1\mathscr{R}_2(R_i)(3\cos^2\theta_i-1)],\\
V^{(1)}_{\Gamma_a^3} = V^{(1)}_{\Gamma_b^3} &= \sum_{i=1}^{N} Q_i[\mathscr{R}_0(R_i)-0{,}1\mathscr{R}_2(R_i)(3\cos^2\theta_i-1)].
\end{aligned} \tag{13}$$

We thus have two different eigenvalues, ε_1 and ε_2, which correspond to two values of the energy of the $np_{3/2}$ level, each of which is doubly degenerate. The splitting of the $np_{3/2|1/2|}$ and $np_{3/2|3/2|}$ levels is

$$\Delta\varepsilon_{np_{3/2}} = \sum_{i=1}^{N} 0{,}2Q_i(3\cos^2\theta_i-1)\left\{\frac{1}{R_i^3}\int_0^{R_i} r^4[g^2(r)+f^2(r)]\,dr + R_i^2\int_{R_i}^{\infty}\frac{1}{r}[g^2(r)+f^2(r)]\,dr.\right. \tag{14}$$

In the nonrelativistic case the increments in the energy are[5]

$$\begin{aligned}
\varepsilon_{xy} &= \sum_{i=1}^{N} Q_i[\mathscr{R}_0(R_i)-0{,}1\mathscr{R}_2(R_i)(3\cos^2\theta_i-1)],\\
\varepsilon_z &= \sum_{i=1}^{N} Q_i[\mathscr{R}_0(R_i)+0{,}2\mathscr{R}_2(R_i)(3\cos^2\theta_i-1)).
\end{aligned} \tag{15}$$

The term

$$E_0 = \sum_{i=1}^{N} Q_i\mathscr{R}_0(R_i),$$

which corresponds to the center of gravity of the level, is the same in the relativistic and nonrelativistic descriptions. The picture of the splitting and the magnitude of the splitting are quite different. In the nonrelativistic approximation, the magnitude of the splitting is larger by a factor of 1.5, to within the difference in the radial integrals.

3. RELATIVISTIC ANGULAR DISTRIBUTION OF THE *K* EMISSION

Let us find the angular distribution of the emission in the course of $np_{3/2} \to 1s$ and $np_{1/2} \to 1s$ transitions for the relativistic case.

For an electric dipole transition from state i to state f, the probability for the emission of a photon with polarization λ into a solid angle $d\Omega_{\mathbf{k}}$ is

$$P_{\mathbf{k}\lambda} = \frac{\omega^3}{\hbar c^3}\frac{d\Omega_k}{2\pi}|\langle\psi_f|\mathbf{e}_{\mathbf{k}}^{(\lambda)}\mathbf{D}|\psi_i\rangle|^2. \tag{16}$$

Here $\omega = kc$, $\mathbf{k}$ is the wave vector, and $\mathbf{e}_{\mathbf{k}}^{(\lambda)}\perp\mathbf{k}$ is the polarization unit vector. The operator representing the electric dipole transition, $\mathbf{D}$, is the dipole-moment operator of the atom in the relativistic case, as it is in the nonrelativistic approximation:[12]

$$\mathbf{D} = e\mathbf{r}. \tag{17}$$

The matrix element in (16) is conveniently written as a scalar product:

$$\langle\psi_f|\mathbf{e}_{\mathbf{k}}^{(\lambda)}\mathbf{r}|\psi_i\rangle = (\mathbf{e}_{\mathbf{k}}^{(\lambda)}\mathbf{r}_{if}), \tag{18}$$

where $\mathbf{e}_{\mathbf{k}}^{(\lambda)}$ depends only on the emission direction and the polarization of the emitted photon, and the matrix element $\mathbf{r}_{if}$ is determined completely by the internal parameters of the emitting atom.

We define two polarization states, putting the vector $\mathbf{e}_{\mathbf{k}}^{(1)}$ in the plane which passes through the z axis and through the vector $\mathbf{k}$, and putting $\mathbf{e}_{\mathbf{k}}^{(2)}$ perpendicular to this plane. If θ and Φ are the spherical angles of the vector $\mathbf{k}$, the coordinates of the vectors $\mathbf{e}_{\mathbf{k}}^{(1)}$ and $\mathbf{e}_{\mathbf{k}}^{(2)}$ are then

$$\begin{gathered}
e_x^{(1)} = \cos\theta\cos\Phi,\quad e_y^{(1)} = \cos\theta\sin\Phi,\quad e_z^{(1)} = -\sin\theta,\\
e_x^{(2)} = -\sin\Phi,\quad e_y^{(2)} = \cos\Phi,\quad e_z^{(2)} = 0.
\end{gathered} \tag{19}$$

We can find the components x_{if}, y_{if}, and z_{if} of the matrix element r_{if} by assuming that the wave functions of the initial and final states are given by (12) with $l = 1, j = 3/2$ and $l = 0, j = 1/2$, respectively. The values of x_{if}, y_{if}, and z_{if} are given to within an inconsequential phase factor in Table I, where the wave function of the final state is $\varphi_{\Gamma^1}^{(1)} = \psi_{0(1/2)-1/2}$. If the final state is described instead by the function $\varphi_{\Gamma^1}^{(2)} = -\psi_{0(1/2)-1/2}$, then the values of $|x_{if}|$, $|y_{if}|$, and $|z_{if}|$ from the first line of this table correspond to the initial state $\varphi_{\Gamma^1}^{(2)} = -\psi_{1(3/2)-1/2}$, and those from the second line correspond to the initial state $\varphi_{\Gamma^1}^{(1)} = \psi_{1(3/2)(1/2)}$. The last two lines of this table do not change. The radial integral $\widetilde{R}$ is

$$\tilde{R} = \int_0^\infty (g_{1s}g_{np_{3/2}} + f_{1s}f_{np_{3/2}})r^3\,dr. \tag{20}$$

We can now calculate the scalar product $(\mathbf{e}_{\mathbf{k}}^{(\lambda)}\mathbf{r}_{if})$ which appears in the expression for the emission probability,

TABLE I. The components $|x_{if}|$, $|y_{if}|$, and $|z_{if}|$ of the matrix element r_{if} in Eq. (18).

Initial state	x_{if}	y_{if}	z_{if}
$\varphi^{(1)}_{\Gamma^1}=\varphi_{1\,3/2\,1/2}$	0	0	$\frac{2^{1/2}}{3}\tilde{R}$
$\varphi^{(2)}_{\Gamma^1}=-\psi_{1\,3/2\,-1/2}$	$\frac{1}{3\cdot 2^{1/2}}\tilde{R}$	$\frac{1}{3\cdot 2^{1/2}}\tilde{R}$	0
$\varphi^{(1)}_{\Gamma^3_a}=\frac{1}{2^{1/2}}(\psi_{1\,3/2\,3/2}+i\psi_{1\,3/2\,-3/2})$	$\frac{1}{2\cdot 3^{1/2}}\tilde{R}$	$\frac{1}{2\cdot 3^{1/2}}\tilde{R}$	0
$\varphi^{(1)}_{\Gamma^3_b}=\frac{1}{2^{1/2}}(-i\psi_{1\,3/2\,3/2}-\psi_{1\,3/2\,-3/2})$	$\frac{1}{2\cdot 3^{1/2}}\tilde{R}$	$\frac{1}{2\cdot 3^{1/2}}\tilde{R}$	0

and we can identify in (16) a factor $\mathbf{A}_{\mathbf{k}}^{(\lambda)}(\theta)$, which contains the dependence on the angle θ:

$$A_{\mathbf{k}}^{(\lambda)}(\theta)=\frac{3}{\tilde{R}^2}|(\mathbf{e}_{\mathbf{k}}^{(\lambda)}\mathbf{r}_{if})|^2. \tag{21}$$

Values of $A_{\mathbf{k}}^{(\lambda)}(\theta)$ are given in Table II for a $\varphi^{(1)}_{\Gamma^1}$ final state. As in Table I, if the final state is described by the wave function $\varphi^{(2)}_{\Gamma^1}$, the values of $A_{\mathbf{k}}^{(\lambda)}$ on the first line in Table II correspond to a $\varphi^{(2)}_{\Gamma^1}$ initial state, and the values of $A_{\mathbf{k}}^{(\lambda)}$ on the second line correspond to a $\varphi^{(1)}_{\Gamma^1}$ initial state.

After we take an average over final states and sum over the polarizations λ, we find the following expressions for the probability for electric dipole emission for the $np_{3/2}\to 1s$ transition:

$$P_{\mathbf{k}}(np_{3/2}\to 1s)$$

$$=\frac{e^2\omega^3}{\hbar c^3}\frac{\tilde{R}^2}{6\pi}d\Omega_{\mathbf{k}}\begin{cases}{}^1/_4({}^2/_3+\sin^2\theta), & \Gamma^1(m_i=\pm{}^1/_2),\\ {}^1/_4(1+\cos^2\theta), & \Gamma_{ab}{}^3(m_i=\pm{}^3/_2).\end{cases} \tag{22}$$

Similar calculations for the transition $np_{1/2}\to 1s$ lead to

$$P_{\mathbf{k}}(np_{1/2}\to 1s)=\frac{e^2\omega^3}{\hbar c^3}\frac{\tilde{R}^2}{6\pi}d\Omega_{\mathbf{k}}\cdot\frac{1}{3},\qquad \Gamma^1(m_i=\pm{}^1/_2). \tag{23}$$

Using nonrelativistic wave functions (we are ignoring the spin) to calculate the matrix elements $\mathbf{r}_{if}$, we find the known[13] angular distribution for the $np\to 1s$ transition:

$$P_{\mathbf{k}}(np\to 1s)=\frac{e^2\omega^3}{\hbar c^3}\frac{\tilde{R}^2}{6\pi}d\Omega_{\mathbf{k}}\begin{cases}{}^1/_2(1+\cos^2\theta) & (m_i=\pm 1),\\ \sin^2\theta & (m_i=0).\end{cases} \tag{24}$$

It can be shown that expressions (22) and (23) are valid for $np_{3/2}\to 1s$ and $np_{1/2}\to 1s$ transitions in a crystal field of any symmetry lower than cubic. This conclusion follows from an analysis of functions which are transformed by irreducible representations of all the crystallographic point groups which are obtained from the irreducible representations of the rotation group with angular momenta $j=3/2$ and $j=1/2$ (Ref. 14). It is also interesting to note that the angular distribution of the emission for M 1 nuclear radiative magnetic transitions between 3/2 and 1/2 levels of identical parity in an axial external field is similar[15] to our expressions (22).

In all the studies of which we are aware (see the review in Ref. 6), experimental data on orientational splitting have been analyzed by means of the nonrelativistic equations (24). When there is a large spin-orbit splitting, as in the case of the inner shells of heavy atoms, the relativistic expressions (22) and (23) must be used. This circumstance changes the values of the splitting $\Delta\varepsilon$ found from the experiments. Let us consider some simple examples of the use of the angular distributions found here.

The energy of the intensity maximum, $E(\theta)$, for a given observation angle can be defined as the average of the energies ε_i of the intensity maxima of the split components of the multiplet (under the condition that the magnitude of the splitting is much smaller than the half-width of the lines of the components):

$$E(\theta)=\frac{\sum_i n_iP_i(\theta)\varepsilon_i}{\sum_i n_iP_i(\theta)}. \tag{25}$$

Here n_i is the degree of degeneracy of level i, and $P_i(\theta)$ is the intensity corresponding to component i.

TABLE II. The quantities $A_{k}^{(\lambda)}(\theta)$ in (21) for various initial states and polarizations λ.

Initial state	$\lambda=1$	$\lambda=2$	Initial state	$\lambda=1$	$\lambda=2$
$\varphi^{(1)}_{\Gamma^1}$	${}^2/_3\sin^2\theta$	0	$\varphi^{(1)}_{\Gamma^3_a}$	${}^1/_4\cos^2\theta$	${}^1/_4$
$\varphi^{(2)}_{\Gamma^1}$	${}^1/_6\cos^2\theta$	${}^1/_6$	$\varphi^{(1)}_{\Gamma^3_b}$	${}^1/_4\cos^2\theta$	${}^1/_4$

Finding the relationship between the shift observed experimentally,

$$\delta E^{\mathrm{obs}}=E_1(\pi/2)-E_2(0),$$

and the level splitting $\Delta\varepsilon = \varepsilon_1 - \varepsilon_2$, and using nonrelativistic angular distribution (24), we have

$$\Delta\varepsilon=2\delta E^{\mathrm{obs}}. \tag{26}$$

When the relativistic expressions (22) and (23) for the angular distribution are used, this relation becomes

$$\Delta\varepsilon=\frac{8}{3}\delta E^{\mathrm{obs}} \tag{27}$$

in the case in which the lines corresponding to the $np_{3/2}$ and $np_{1/2}$ levels can be resolved experimentally or

$$\Delta\varepsilon=4\delta E^{\mathrm{obs}} \tag{28}$$

in the case in which the $np_{3/2}$ and $np_{1/2}$ levels cannot be resolved.

Consequently, the values of $\Delta\varepsilon$ found from experimental data with the help of (27) and (28) may differ from the values found from (26) by a factor ranging from 4/3 to 2.

As we have already mentioned, the cases we have discussed are simple examples of determining the splitting of the components of a multiplet from experimental data through the use of the relativistic angular distributions which we have derived for the emission intensity. Expressions (22) and (23), derived here, can be used with existing programs[16] for a first-principles calculation of the shape and the parameters of the lines of the individual components of a multiplet as well as complete theoretical x-ray spectra with a given polarization or a given direction for the case of pure *jj* coupling.

The case in which the splitting by the crystal field, $\Delta\varepsilon$, is comparable to the spin-orbit interaction requires a special analysis.

4. CALCULATION OF THE SPLITTING OF CORE *p* LEVELS OF A NIOBIUM ION IN A LITHIUM METANIOBATE SINGLE CRYSTAL

Let us examine a specific example of the calculation of level splitting in an anisotropic crystal. The splitting of the $np_{3/2}$ level ($n = 2, 3, 4$) of the niobium ion in a $LiNbO_3$ single crystal was calculated from (14). The effective charges at the ligands, Q_i, were taken from Ref. 17: $Q_{\mathrm{Nb}} = 3.28$, $Q_{\mathrm{Li}} = 0.89$, $Q_0 = -1.39$. The radial electron wave functions $g(r)$ and $f(r)$ of a central niobium ion were found through numerical integration of Eqs. (5) for the free Nb^{4+} ion: $np^3_{3/2}4d^{\,4}_{3/2}$ (Ref. 16). As $\widetilde{V}(r)$ we used the potential for the Nb^{4+} ion with a vacancy in the *np* shell, put in a self-consistent form by the relativistic Dirac-Fock-Slater method. This approach corresponds to incorporating the relaxation of the central niobium ion after a vacancy forms as the result of an x-ray transition. Incorporating the relaxation changes the radial integrals in (14) by ~5%.

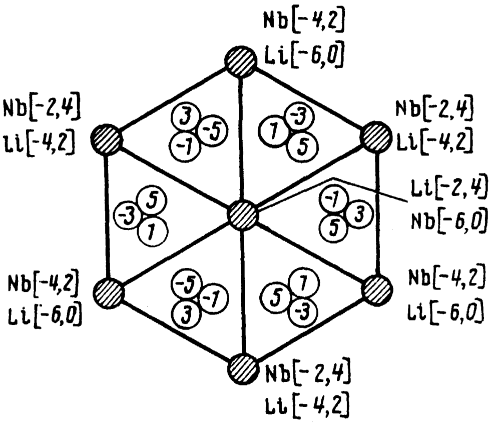

FIG. 1. Positions of niobium, lithium, and oxygen ions in the $LiNbO_3$ crystal. The plane of this figure is perpendicular to the symmetry axis of the crystal. At the center and vertices of the hexagonal cell are niobium and lithium ions; the numerals in the labels specify the layers in which these ions lie. In the inner part of the hexagonal cell there are oxygen ions, which form a regular triangle in each layer. The numbers in circles specify the layer with the corresponding oxygen ions.

The positions of the ions in the crystal lattice, i.e., the quantities R_i and θ_i in (14), were determined from data found on lithium metaniobate by neutron diffraction[18] and x-ray diffraction.[19,20]

The choice of the complex of ligand ions over which to sum in (14) is related to the structure of the $LiNbO_3$ crystal.

TABLE III. Partial splittings $\Delta\varepsilon^I_{4p3/2}$ (in meV) corresponding to the various layers of the complex.

I	R^I_V, a.u.	$\Delta\varepsilon^I_{4p_{3/2}}$, meV	$\sum_I \Delta\varepsilon^I_{4p_{3/2}}$, meV	I	R^I_V, a.u.	$\Delta\varepsilon^I_{4p_{3/2}}$, meV	$\sum_I \Delta\varepsilon^I_{4p_{3/2}}$, meV
10	21,8	49	—3	0	0,0	—459	71
9	20,1	—52		—1	1,7	669	
8	17,5	56	—3	—2	4,4	—169	
7	15,8	—59		—3	6,0	—48	
6	13,1	63	—3	—4	8,7	73	+5
5	11,4	—66		—5	10,4	—68	
4	8,7	61		—6	13,1	64	+4
3	7,0	—60		—7	14,8	—60	
2	4,4	—36		—8	17,5	57	+3
1	2,7	114		—9	19,2	—54	

Note. Here R^I_V is the distance from layer I (if I is even, it is the distance from the plane containing the niobium ions) to the $I = 0$ layer. The sums $\Sigma_I \Delta\varepsilon^I_{4p_{3/2}}$ include a summation over two layers for $I \geqslant 5$ and for $I \leqslant -4$. For $-3 \leqslant I \leqslant 4$, the contributions from eight layers are summed.

TABLE IV. Splittings $\Delta\varepsilon_{4p3/2}$ (in meV) for complexes I–V, containing various numbers of ligand ions. Here N_M and N_O are the numbers of ions in a metal layer and in an oxygen layer, respectively.

Complex	N_M	N_O	N_C	N	R_h, a.u.	$\Delta\varepsilon_{4p_{3/2}}$, MeV
I	4 (6)	6 (9)	6	35	8,1	136
II	12 (13)	18	12	180	11,3	47
III	36 (37)	54	20	900	20,2	68
IV	72 (73)	108	24	2160	29,7	73
V	120 (121)	180	24	3600	39,3	75

At room temperature, lithium metaniobate crystals consist of layers of oxygen ions in approximately hexagonal close packing. A third of the octahedral voids formed by the oxygen ions are filled by niobium ions, another third are filled by lithium ions, and the rest are vacant. All the oxygen octahedra are distorted. There are two types of metal-oxygen distances. Figure 1 shows the positions of the oxygen and metal ions in each of the 12 layers $I = -6, -5, \ldots, 4, 5$ in a unit cell. Each layer with odd I contains oxygen ions in hexagonal cells at the vertices of regular triangles. Each metal layer (even I) contains niobium and lithium ions at the vertices and centers of hexagonal cells. The niobium and lithium ions are in two parallel planes, separated by a distance of 1.3 a.u. (We are assuming that the central niobium ion is at the center of the $I = 0$ layer.)

The following conditions were considered in the selection of the complex of ions for the calculation. First, we included all those ions in a layer which were closer to the center of the layer than a given distance R_h for a given complex. Second, the complex had to be electrically neutral, so the values of R_h were chosen in such a way that the charge of the metal layer was approximately the same in absolute value as the charge of the oxygen layer, and the number of layers in the complex was even.

These conditions were taken into account in the summation in (14) over the layers. In other words, we calculated the partial splittings $\Delta\varepsilon^{I}_{np_{3/2}}$ corresponding to the contributions of the layer of index I to the total splitting $\Delta\varepsilon_{np_{3/2}}$. Table III shows partial splittings $\Delta\varepsilon_{4p_{3/2}}$ for a complex of 20 layers. Each metal layer has 60 (or 61) niobium ions and 61 (or 60) lithium ions; each oxygen layer has 180 oxygen ions; and the distance R_h is 39 a.u. We see from Table III that the contribution $\Delta\varepsilon_{4p_{3/2}}$ is comparable to the total splitting for all the layers considered. For layers sufficiently far from the central ion, however, these contributions cancel out for each pair of one oxygen layer and one metal layer and also for pairs which are positioned symmetrically with respect to layer 0. The value of $\Delta\varepsilon_{4p_{3/2}}$ is dominated ($\sim 95\%$) by the eight layers closest to layer 0.

Calculations were carried out for five complexes with various numbers (N) of lattice ions by this method of conditional summation over ions. The splittings $\Delta\varepsilon_{np_{3/2}}$ found for these complexes converge on their asymptotic values with increasing N. Table IV shows data on the structure of the complexes, along with the corresponding values of $\Delta\varepsilon_{4p_{3/2}}$. We see from this table that for complexes I and II, which contain 35 and 180 ions, respectively, the splitting $\Delta\varepsilon_{4p_{3/2}}$ oscillates, differing by a factor of nearly 2 from its asymptotic value. For complexes IV (2160 ions) and V (3600 ions), the value of $\Delta\varepsilon_{4p_{3/2}}$ are essentially the same.

The theoretical values and experimental values[21] of the splitting of the $np_{3/2}$ levels of the niobium atom in a $LiNbO_3$ single crystal are

$$\Delta\varepsilon^{\text{theor}}_{{}^2P_{3/3}} = 1\ \text{meV},\quad \Delta\varepsilon^{\text{theor}}_{{}^3P_{3/3}} = 10\ \text{meV},\quad \Delta\varepsilon^{\text{theor}}_{{}^4P_{3/3}} = 75\ \text{meV},$$

$$\Delta\varepsilon^{\text{theor}}_{{}^2P_{3/3}} = 5 \pm 2\ \text{meV},\quad \Delta\varepsilon^{\text{theor}}_{{}^3P_{3/3}} = 13 \pm 6\ \text{meV},$$

$$\Delta\varepsilon^{\text{theor}}_{{}^4P_{3/3}} = 160 \pm 8\ \text{meV}.$$

Despite the crudeness of the point-ion model, the agreement between the theoretical results and the experimental data of Ref. 21, found through a study of the orientation dependence of the energies of K emission lines, can be judged satisfactory. A simple improvement in this model through the incorporation of the screening of the point ions—this approach would effectively correspond to reducing the size of the cluster under consideration, according to Table IV—should improve the results for $\Delta\varepsilon_{4p_{3/2}}$.

Corresponding estimates of the effect of the anisotropy of the crystal on the level splitting can be found for the new, highly anisotropic phases of high T_c superconductors (of the perovskite type) which are structurally related to lithium metaniobate. Experimental studies in this direction have already appeared; e.g., there has been a study of the polarized x-ray spectra of the Cu L_3 absorption edge of $YBa_2Cu_3O_{7-\delta}$ single crystals.[22] We have carried out a more thorough theoretical study for the L spectra, using the same method as was used for the K spectra.

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