Optical spin orientation in crystals with diamond structure

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In a new type of photoemission experiment, spin orientation of the photoelectrons is achieved by the optical excitation process. The spin polarization depends only on the symmetry of the states involved. In this paper the method of optical spin orientation is applied to electronic states belonging to the important nonsymmorphic space group of the diamond lattice. Tables of Clebsch-Gordan coefficients at the special symmetry points X and W and symmetry line Z of the Brillouin zone are given. They contain the necessary information to derive the spin polarization. For the other parts of the Brillouin zone it is shown that the already published tables for the point groups are applicable.

I. INTRODUCTION

The introduction of the electron spin polarization in photoemission has led to new insights into the electronic band structure of solids. Originally, the method was developed to investigate the spin-dependent electronic structure of magnetic solids, the most intensively studied material being nickel[1,2]: It was possible to detect the negative spin polarization at the Fermi level, certainly a major experimental breakthrough in the field of magnetism in the last decade.

At the same time it became clear that the method of spin-polarized photoemission can be extended to materials with unpolarized ground states. There the polarization of the photoelectrons must first be created by the optical excitation process. This is called optical spin orientation. The measurement of the spin polarization bears distinct advantages[3] in this case also: The hybridization of energy bands becomes directly measurable, the resolution of energetically closely spaced transitions is improved, and the assignment of the observed transitions in a band structure becomes much simpler than in conventional angular- and energy-resolved photoemission.

Sign and magnitude of the light-induced polarization are determined solely by the symmetry of the electron wave functions involved in the transitions[4]: The knowledge of the radial part is not needed. Therefore, the whole subject falls into the domain of group theory: The relative weight of the up and down spins in the excited wave function is given by the Clebsch-Gordan coefficients.[3,4] The purpose of this paper is to apply the method of optical spin orientation to a particularly important class of materials, namely, those with the diamond structure. The diamond structure belongs to a nonsymmorphic space group. This implies that the light-induced spin polarization cannot in general be dealt with using point-group symmetries, in contrast to the cubic Bravais lattices.[4] The Clebsch-Gordan coefficients necessary for deriving the spin polarization in crystals with diamond structure are still missing. In this paper they are presented for the symmetry points X and W and along the symmetry line Z of the Brillouin zone; see Fig. 1. For the other symmetry locations it is shown that the point-group tables—e.g., of Ref. 5—can be used.

II. USE OF THE CLEBSCH-GORDAN COEFFICIENTS FOR THE CALCULATION OF THE LIGHT-INDUCED POLARIZATION: AN EXAMPLE

Since the electric field of the radiation interacts only with the orbital part of an electron wave function, spin orientation requires the presence of spin-orbit coupling in the solid. In this case up and down spins no longer have the same orbital part, and a selective excitation may occur. In the presence of spin-orbit interaction the symmetry of an electron wave function $\psi_{\vec{k}}(\vec{r})$ is described by an irreducible representation of the double group of the wave vector $\vec{k}$. $\psi_{\vec{k}}(\vec{r})$ consists of orbital and spin functions properly combined to possess the correct double-group symmetry. The symmetry-adapted wave functions are built up by means of the Clebsch-Gordan coefficients, given for the points X and W and line Z in Tables I—III.

As an example of the application of these tables, consider transitions from the initial states of symmetry W_7^1 to the final states of symmetry $W_4^2W_6^2$ (see Fig. 2). The subscript indicates the double-group representation, the superscript the single-group representation from which the orbital parts of the wave functions are derived. The two states of W_7^1 symmetry, for instance, are found in Table II for the reduction of $W^1\otimes D_{1/2},D_{1/2}$ being the spin-$\frac{1}{2}$ representation of the elements of the space group. The representations $W_4^2W_6^2$ are taken together because they are degenerate by time-reversal symmetry.[6]

The perturbation operator inducing direct optical transitions is $\vec{a}_0\cdot\vec{p}$, where $\vec{p}=(\hbar/i)(\partial/\partial x,\partial/\partial y,\partial/\partial z)$, and $\vec{a}_0$ is the polarization vector of the light.[7] According to the so-called dipole-selection rules, some transitions may be strictly forbidden by symmetry. Let Γ^f, Γ^r, Γ^i be the irreducible representations according to which the final state, the radiation operator, and the initial state, respectively, transform. If Γ^f is not contained in the decompo-

sition of $\Gamma^r \otimes \Gamma^i$, then the transition $\Gamma^i \rightarrow \Gamma^f$ is not allowed. Table IV gives the dipole-selection rules for transitions occurring at symmetry points X and W and line Z. At the top are the initial states, and on the left-hand side the irreducible representations of the group of the wave vector according to which p_x, p_y, and p_z transform. The decomposition of $\Gamma^r \otimes \Gamma^i$ is contained in this table.

As shown elsewhere,[4] circularly polarized light is necessary for obtaining nonvanishing spin polarization. For the transition $W_7^1 \rightarrow W_4^2 W_6^2$ we choose right-hand circularly-polarized light propagating in the $-x$ direction (see Fig. 1): $\vec{a}_0 \cdot \vec{p} = p_y - ip_z$. Since the transition is not forbidden we can proceed further with the calculation of the spin polarization. The quantities of interest are now the matrix elements of the operator $p_y - ip_z$ between the various states of symmetry W_7^1 and $W_4^2 W_6^2$. Consider, for instance, $\langle \psi_4 | (p_y - ip_z) | \psi_2^7 \rangle$. As in Ref. 5, in the case of one-dimensional representations the subscript to a wave function denotes the irreducible representation. For multidimensional representations, the irreducible representation is indicated by a superscript and the various basis functions are denoted by subscripts. p_y and p_z belong to W_3^r; see Table IV. Since the spin functions $v_{1/2}$ and $v_{-1/2}$ are orthonormal, it follows the equality

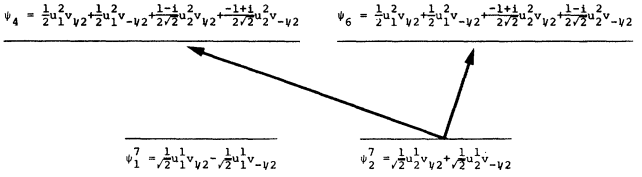

FIG. 2. Level scheme for transitions $W_7^1 \rightarrow W_4^2 W_6^2$ by right-hand circularly-polarized light at the W point. Indicated by arrows are the transitions with nonvanishing matrix element. The notation used is explained in the text.

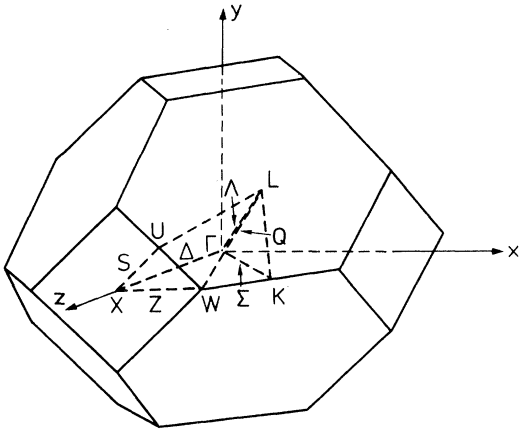

FIG. 1. Brillouin zone for the fcc lattice. Symmetry points and lines are as follows:

Point	Coordinates
Γ	(0,0,0)
K	$(2\pi/a)(\frac{3}{4},0,\frac{3}{4})$
L	$(2\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
U	$(2\pi/a)(\frac{1}{4},\frac{1}{4},1)$
W	$(2\pi/a)(\frac{1}{2},0,1)$
X	$(2\pi/a)(0,0,1)$
Line	**Coordinates, $0<\kappa<1$**
Δ	$(2\pi/a)(0,0,\kappa)$
Λ	$(2\pi/a)(\frac{1}{2}\kappa,\frac{1}{2}\kappa,\frac{1}{2}\kappa)$
Σ	$(2\pi/a)(\frac{3}{4}\kappa,0,\frac{3}{4}\kappa)$
Q	$(2\pi/a)(\frac{1}{2},\frac{1}{2}(1-\kappa),\frac{1}{2}(1+\kappa))$
S	$(2\pi/a)(\frac{1}{4}\kappa,\frac{1}{4}\kappa,1)$
Z	$(2\pi/a)(\frac{1}{2}\kappa,0,1)$

TABLE I. Clebsch-Gordan coefficients for the decomposition of the direct product between the single-group representations of point X and $D_{1/2}$. Columns are labeled by the product functions and the rows by the irreducible linear combinations. As in Ref. 5, in the case of one-dimensional representations the subscript to a wave function denotes the irreducible representation. For multidimensional representations, the subscript denotes the various basis functions of an irreducible representation and the superscript denotes (where necessary) the irreducible representation. $\gamma = \frac{1}{2}(1+i)$.

$X_1 \otimes D_{1/2} = X_5$	$u_1 v_{1/2}$	$u_1 v_{-1/2}$	$u_2 v_{1/2}$	$u_2 v_{-1/2}$
ψ_1	1	0	0	0
ψ_2	0	1	0	0
ψ_3	0	0	1	0
ψ_4	0	0	0	1
$X_2 \otimes D_{1/2} = X_5$	$u_1 v_{1/2}$	$u_1 v_{-1/2}$	$u_2 v_{1/2}$	$u_2 v_{-1/2}$
ψ_1	0	0	i	0
ψ_2	0	0	0	$-i$
ψ_3	i	0	0	0
ψ_4	0	$-i$	0	0
$X_3 \otimes D_{1/2} = X_5$	$u_1 v_{1/2}$	$u_1 v_{-1/2}$	$u_2 v_{1/2}$	$u_2 v_{-1/2}$
ψ_1	0	γ	0	$i\gamma$
ψ_2	$i\gamma$	0	γ	0
ψ_3	0	γ	0	$-i\gamma$
ψ_4	$i\gamma$	0	$-\gamma$	0
$X_4 \otimes D_{1/2} = X_5$	$u_1/v_{1/2}$	$u_1 v_{-1/2}$	$u_2 v_{1/2}$	$u_2 v_{-1/2}$
ψ_1	0	γ	0	$i\gamma$
ψ_2	$i\gamma$	0	γ	0
ψ_3	0	$-\gamma$	0	$i\gamma$
ψ_4	$-i\gamma$	0	γ	0

TABLE II. Clebsch-Gordan coefficients for the decomposition of the direct product between the single-group representations of point W and $D_{1/2}$. Columns are labeled by the product functions and the rows by the irreducible linear combinations. As in Ref. 5, in the case of one-dimensional representations the subscript to a wave function denotes the irreducible representation. For multidimensional representations, the subscript denotes the various basis functions of an irreducible representation and the superscript denotes (where necessary) the irreducible representation.

$W_1\otimes D_{1/2}$ $=W_3+W_5+W_7$	$u_1v_{1/2}$	$u_1v_{-1/2}$	$u_2v_{1/2}$	$u_2v_{-1/2}$
ψ_3	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{-1+i}{2\sqrt{2}}$	$\frac{1-i}{2\sqrt{2}}$
ψ_5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1-i}{2\sqrt{2}}$	$\frac{-1+i}{2\sqrt{2}}$
ψ_1^7	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	0	0
ψ_2^7	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$

$W_2\otimes D_{1/2}$ $=W_4+W_6+W_7$	$u_1v_{1/2}$	$u_1v_{-1/2}$	$u_2v_{1/2}$	$u_2v_{-1/2}$
ψ_4	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1-i}{2\sqrt{2}}$	$\frac{-1+i}{2\sqrt{2}}$
ψ_6	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{-1+i}{2\sqrt{2}}$	$\frac{1-i}{2\sqrt{2}}$
ψ_1^7	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
ψ_2^7	$\frac{i}{\sqrt{2}}$	$-\frac{i}{\sqrt{2}}$	0	0

$$\langle\psi_4\,|\,(p_y-ip_z\,|\,\psi_2^7\rangle = \frac{1}{\sqrt{2}}[\langle u_1^2\,|\,p_y\,|\,u_2^1\rangle + i\langle u_1^2\,|\,(-p_z)\,|\,u_2^1\rangle]\,.$$

In order to calculate the resulting matrix elements on the right-hand side of this equality we make use of the Wigner-Eckart theorem developed for space groups by Koster.[8] According to this theorem, such matrix elements are all equal to the same constant $c(W_1,W_3^r,W_2)$, dependent only on the irreducible representations involved, multiplied by the complex conjugate of a Clebsch-Gordan coefficient.[9] For instance, the Clebsch-Gordan coefficient appropriate for $\langle u_1^2\,|\,p_y\,|\,u_2^1\rangle$ is the factor accompanying the product function $u_y^3u_2^1$ in the expansion of u_1^2 in terms of the product functions $u_y^3u_1^1,u_y^3u_2^1,u_{-z}^3u_1^1,u_{-z}^3u_2^1$. From Table VIII we see that this factor is $1/\sqrt{2}$. Tables V–XI give all the Clebsch-Gordan coefficients necessary for the calculation of matrix elements of direct optical transitions at symmetry points X and W and line Z. For the specific example studied we obtain, referring to Table VIII for $W_3^r\otimes W_1$,

$$M_{7\to4}:=\langle\psi_4\,|\,(p_y-ip_z)\,|\,\psi_2^7\rangle=c(W_1,W_3^r,W_2)$$

and

$$M_{7\to6}:=\langle\psi_6\,|\,(p_y-ip_z)\,|\,\psi_2^7\rangle=c(W_1,W_3^r,W_2)\,.$$

The remaining matrix elements vanish. Therefore only

TABLE III. Clebsch-Gordan coefficients for the decomposition of the direct product between the single-group representation of line Z and $D_{1/2}$. Columns are labeled by the product functions and the rows by the irreducible linear combinations. As in Ref. 5, in the case of one-dimensional representations the subscript to a wave function denotes the irreducible representation. $\delta=(1-i)/2\sqrt{2}$.

$Z_1\otimes D_{1/2}$ $=Z_2+Z_3+Z_4+Z_5$	$u_1v_{1/2}$	$u_1v_{-1/2}$	$u_2v_{1/2}$	$u_2v_{-1/2}$
ψ_2	δ	$-\delta$	$-i\delta$	$-i\delta$
ψ_3	δ	$-\delta$	$i\delta$	$i\delta$
ψ_4	δ	δ	$-i\delta$	$i\delta$
ψ_5	δ	δ	$i\delta$	$-i\delta$

TABLE IV. Allowed optical transitions at symmetry points at X and W and along line Z. On the left, the representations according to which p_x,p_y,p_z transform are indicated. At the top are the initial states. The decomposition of $\Gamma^r\otimes\Gamma^i$ is given in the table.

	X_1	X_2	X_3	X_4	X_5		
$X_4'^r:p_z$	X_1	X_2	X_4	X_3	X_5		
$X_5'^r:p_x,p_y$	X_3+X_4	X_3+X_4	X_1+X_2	X_1+X_2	$2X_5$		
	W_1	W_2	W_3	W_4	W_5	W_6	W_7
$W_2'^r:p_x$	W_2	W_1	W_6	W_5	W_4	W_3	W_7
$W_3^r:p_y,-p_z$	W_1+W_2	W_1+W_2	W_7	W_7	W_7	W_7	$W_3+W_4+W_5+W_6$
	Z_1	Z_2	Z_3	Z_4	Z_5		
$Z_1^r:p_x$	Z_1	Z_2	Z_3	Z_4	Z_5		
$Z_3^r:p_z$	Z_1	Z_5	Z_4	Z_3	Z_2		
$Z_4^r:p_y$	Z_1	Z_4	Z_5	Z_2	Z_3		

TABLE V. Clebsch-Gordan coefficients for the decomposition of the direct product between the radiation representation $X_4'^r$ and single- or double-group representations. Notation as in Tables I–III.

$X_4'^r\otimes X_1$ $=X_1$	$u_z v_1$	$u_z v_2$	$X_4'^r\otimes X_2$ $=X_2$	$u_z v_1$	$u_z v_2$
ψ_1	0	1	ψ_1	0	1
ψ_2	−1	0	ψ_2	−1	0
$X_4'^r\otimes X_3$ $=X_4$	$u_z v_1$	$u_z v_2$	$X_4'^r\otimes X_4$ $=X_3$	$u_z v_1$	$u_z v_2$
ψ_1	1	0	ψ_1	1	0
ψ_2	0	−1	ψ_2	0	−1

$X_4'^r\otimes X_5$ $=X_5$	$u_z v_1$	$u_z v_2$	$u_z v_3$	$u_z v_4$
ψ_1	0	0	1	0
ψ_2	0	0	0	1
ψ_3	−1	0	0	0
ψ_4	0	−1	0	0

electrons with wave function ψ_2^7 may be excited. After the excitation they possess the final-state wave function

$$|f\rangle=\frac{M_{7\to4}\psi_4+M_{7\to6}\psi_6}{(|M_{7\to4}|^2+|M_{7\to6}|^2)^{1/2}}=\frac{1}{\sqrt{2}}\frac{c(W_1,W_3^r,W_2)}{|C(W_1,W_3^r,W_2)|}u_1^2(v_{1/2}+v_{-1/2})\ . \quad (2.1)$$

The intensity of the transition to this final state is given by

$$|M_f|^2=|M_{7\to4}|^2+|M_{7\to6}|^2=2|c(W_1,W_3^r,W_2)|^2\ .$$

The polarization of this final state is $\vec{P}=\langle f|\vec{\sigma}|f\rangle=(1,0,0)$, $\vec{\sigma}$ being the polarization operator, which is identical to the Pauli matrices for spin-$\frac{1}{2}$ particles. As a result, electrons having made the transition $W_7^1\to W_4^2W_4^2$ are 100% polarized along the x axis.

From this example it is evident that the Wigner-Eckart constant $c(W_1,W_3^r,W_2)$ cancels out in the calculation of $\vec{P}$. This result applies generally, even when degenerate final states are reached simultaneously.[4] In this last case the polarization is given by

$$\vec{P}=\left[\sum_f |M_f|^2\vec{P}_f\right]\Big/\left[\sum_f |M_f|^2\right]\ .$$

As a consequence, the explicit functional dependence of the electron wave functions—determining the Wigner-Eckart constant—is not needed for the calculation of the polarization, which therefore becomes a particularly useful experimental quantity directly accessible to rigorous group-theoretical arguments.

III. METHOD OF CALCULATION OF CLEBSCH-GORDAN COEFFICIENTS FOR SPACE GROUPS

The procedure for constructing Clebsch-Gordan coefficients requires an explicit knowledge of the matrix elements of the irreducible representations of $G_{\vec{k}}$, the group of the wave vector $\vec{k}$. $G_{\vec{k}}$ is the subgroup of the whole space group consisting of all operations which leave $\vec{k}$ unchanged. The elements of $G_{\vec{k}}$ are of the form $\{R\,|\,\vec{\tau}+\vec{f}_R\}$, where the rotation R has the property that $R\vec{k}=\vec{k}+\vec{K}$, where $\vec{K}$ is a reciprocal-lattice vector (which may be zero), $\vec{\tau}$ is a primitive translation, and $\vec{f}_R$ is a nonprimitive translation associated with R (if any exists). $\vec{f}_R$ is always zero for symmorphic space groups: As a consequence, $G_{\vec{k}}$ is a point group (apart from the primitive translations). In nonsymmorphic space groups such as O_h^7 ($Fd3m$), the space group of the diamond lattice, some rotations are associated with nonprimitive translations, and the similarity with point groups breaks down. Actually, the diamond lattice contains equivalent atoms in the unit cell at (0,0,0) and $(a/4)(1,1,1)$, a being the lattice constant. It can be thought of as consisting of two fcc lattices displaced with respect to each other by the vector $(a/4)(1,1,1)$. Therefore, those elements which are associated with the inversion operation at $(a/8)(1,1,1)$—just the middle point between the two atoms in the unit cell—contain the fractional translation $\vec{f}_R=(a/4)(1,1,1)$.

Let Γ^γ be contained in the decomposition of the direct product $\Gamma^\alpha\otimes\Gamma^\beta$. The application of the matrix[10]

$$\sum_{\{R\,|\,\vec{\tau}+\vec{f}_R\}\in G_{\vec{k}}}(\bar{\Gamma}^\gamma_{kl}\Gamma^\alpha\otimes\Gamma^\beta)(\{R\,|\,\vec{\tau}+\vec{f}_R\}) \quad (3.1)$$

TABLE VI. Clebsch-Gordan coefficients for the decomposition of the direct product between the radiation representation $X_5'^r$ and single- or double-group representations. Notation as in Tables I–III. $\alpha=\frac{1}{2}$.

$X_5'^r\otimes X_1$ $=X_3+X_4$	u_xv_1	u_xv_2	u_yv_1	u_yv_2
ψ_1^3	α	$-\alpha$	α	$-\alpha$
ψ_2^3	α	α	$-\alpha$	$-\alpha$
ψ_1^4	α	α	α	α
ψ_2^4	α	$-\alpha$	$-\alpha$	α

$X_5'^r\otimes X_2$ $=X_3+X_4$	u_xv_1	u_xv_2	u_yv_1	u_yv_2
ψ_3^1	α	$-\alpha$	$-\alpha$	α
ψ_2^3	α	α	α	α
ψ_1^4	α	α	$-\alpha$	$-\alpha$
ψ_2^4	α	$-\alpha$	α	$-\alpha$

$X_5'^r\otimes X_3$ $=X_1+X_2$	u_xv_1	u_xv_2	u_yv_1	u_yv_2
ψ_1^1	α	α	α	$-\alpha$
ψ_2^1	$-\alpha$	α	$-\alpha$	$-\alpha$
ψ_1^2	α	α	$-\alpha$	α
ψ_2^2	$-\alpha$	α	α	α

$X_5'^r\otimes X_4$ $=X_1+X_2$	u_xv_1	u_xv_2	u_yv_1	u_yv_2
ψ_1^1	α	α	α	$-\alpha$
ψ_2^1	α	$-\alpha$	α	α
ψ_1^2	α	α	$-\alpha$	α
ψ_2^2	α	$-\alpha$	$-\alpha$	$-\alpha$

$X_5'^r\otimes X_5$ $=2X_5$	u_xv_1	u_xv_2	u_xv_3	u_xv_4	u_yv_1	u_yv_2	u_yv_3	u_yv_4
ψ_1^5	0	$\frac{i}{\sqrt{2}}$	0	0	0	$\frac{1}{\sqrt{2}}$	0	0
ψ_2^5	$\frac{i}{\sqrt{2}}$	0	0	0	$\frac{-1}{\sqrt{2}}$	0	0	0
ψ_3^5	0	0	0	$\frac{-i}{\sqrt{2}}$	0	0	0	$\frac{-1}{\sqrt{2}}$
ψ_4^5	0	0	$\frac{-i}{\sqrt{2}}$	0	0	0	$\frac{1}{\sqrt{2}}$	0
ϕ_1^5	0	0	0	$\frac{-1}{\sqrt{2}}$	0	0	0	$\frac{-i}{\sqrt{2}}$
ϕ_2^5	0	0	$\frac{1}{\sqrt{2}}$	0	0	0	$\frac{-i}{\sqrt{2}}$	0
ϕ_3^5	0	$\frac{1}{\sqrt{2}}$	0	0	0	$\frac{i}{\sqrt{2}}$	0	0
ϕ_4^5	$\frac{-1}{\sqrt{2}}$	0	0	0	$\frac{i}{\sqrt{2}}$	0	0	0

to a vector contained in the space spanned by $\Gamma^\alpha\otimes\Gamma^\beta$ leads to a vector $\psi_{k,l}^\gamma$, which transforms according to the k column of the irreducible representation Γ^γ. By varying the index k in (3.1), the whole set of basis functions for Γ^γ is obtained.

In the case that the representation Γ^γ occurs $n>1$ times in the decomposition of $\Gamma^\alpha\otimes\Gamma^\beta$, the various sets of basis functions with symmetry Γ^γ are obtained by repeating the above calculation n times, each time for a different l value. The factors $U_{ijk,l}^{\alpha\beta\gamma}$ in the expansion of $\psi_{k,l}^\gamma$ in terms

TABLE VII. Clebsch-Gordan coefficients for the decomposition of the direct product between the radiation representation $W_2'^r$ and single- or double-group representations. Notation as in Tables I–III.

$W_2'^r \otimes W_1 = W_2$	$u_x v_1$	$u_x v_2$	$W_2'^r \otimes W_2 = W_1$	$u_x v_2$	$u_x v_2$
ψ_1	1	0	ψ_1	1	0
ψ_2	0	1	ψ_2	0	1

$W_2'^r \otimes W_k$ $(k=3,4,5,6)$		$W_2'^r \otimes W_7 = W_7$	$u_x v_1$	$u_x v_2$
	i	ψ_1	1	0
		ψ_2	0	-1

TABLE VIII. Clebsch-Gordan coefficients for the decomposition of the direct product between the radiation representation W_3^r and single- or double-group representations. Notation as in Tables I–III. $\beta = 1/\sqrt{2}$.

$W_3^r \otimes W_1 = W_1 + W_2$	$u_y v_1$	$u_y v_2$	$u_{-z} v_1$	$u_{-z} v_2$
ψ_1^1	0	β	0	$-i\beta$
ψ_2^1	$i\beta$	0	$-\beta$	0
ψ_1^2	0	β	0	$i\beta$
ψ_2^2	$i\beta$	0	β	0

$W_3^r \otimes W_2 = W_1 + W_2$	$u_y v_1$	$u_y v_2$	$u_{-z} v_1$	$u_{-z} v_2$
ψ_1^1	0	β	0	$i\beta$
ψ_2^1	$i\beta$	0	β	0
ψ_1^2	0	β	0	$-i\beta$
ψ_2^2	$i\beta$	0	$-\beta$	0

$W_3^r \otimes W_3 = W_7$	$u_y v_1$	$u_{-z} v_1$	$W_3^r \otimes W_4 = W_7$	$u_y v_1$	$u_{-z} v_1$
ψ_1	$\frac{1}{\sqrt{2}}$	$-\frac{i}{\sqrt{2}}$	ψ_1	$\frac{1}{\sqrt{2}}$	$\frac{i}{\sqrt{2}}$
ψ_2	$\frac{-1-i}{2}$	$\frac{1-i}{2}$	ψ_2	$\frac{1+i}{2}$	$\frac{1-i}{2}$

$W_3^r \otimes W_5 = W_7$	$u_y v_1$	$u_{-z} v_1$	$W_3^r \otimes W_6 = W_7$	$u_y v_1$	$u_{-z} v_1$
ψ_1	$\frac{1}{\sqrt{2}}$	$-\frac{i}{\sqrt{2}}$	ψ_1	$\frac{1}{\sqrt{2}}$	$\frac{i}{\sqrt{2}}$
ψ_2	$\frac{1+i}{2}$	$\frac{-1+i}{2}$	ψ_2	$\frac{-1-i}{2}$	$\frac{-1+i}{2}$

$W_3^r \otimes W_7 = W_3 + W_4 + W_5 + W_6$	$u_y v_1$	$u_y v_2$	$u_{-z} v_1$	$u_{-z} v_2$
ψ_3	$\frac{1}{2}$	$\frac{-1+i}{2\sqrt{2}}$	$\frac{i}{2}$	$\frac{1+i}{2\sqrt{2}}$
ψ_4	$\frac{1}{2}$	$\frac{1-i}{2\sqrt{2}}$	$\frac{-i}{2}$	$\frac{1+i}{2\sqrt{2}}$
ψ_5	$\frac{1}{2}$	$\frac{1-i}{2\sqrt{2}}$	$\frac{i}{2}$	$\frac{-1-i}{2\sqrt{2}}$
ψ_6	$\frac{1}{2}$	$\frac{-1+i}{2\sqrt{2}}$	$\frac{-i}{2}$	$\frac{-1-i}{2\sqrt{2}}$

TABLE IX. Clebsch-Gordan coefficients for the decomposition of the direct product between the radiation representation Z_1^r and single- or double-group representations. Notation as in Tables I–III.

$Z_1^r \otimes Z_1$ $= Z_1$	$u_x v_1$	$u_x v_2$	$Z_1^r \otimes Z_k$ $(k=2,3,4,5)$	
ψ_1	1	0		i
ψ_2	0	1		

TABLE XI. Clebsch-Gordan coefficients for the decomposition of the direct product between the radiation representation Z_4^r and single- or double-group representations. Notation as in Tables I–III.

$Z_4^r \otimes Z_1$ $= Z_1$	$u_y v_1$	$u_y v_2$	$Z_4^r \otimes Z_k$ $(k=2,3,4,5)$	
ψ_1	0	i		i
ψ_2	$-i$	0		

of the product functions $\psi_i^\alpha \psi_j^\beta$ are the Clebsch-Gordan coefficients: They are chosen so that all wave functions are normalized:

$$\psi_{k,l}^\gamma = \sum_{i,j} U_{ijk,l}^{\alpha\beta\gamma} \psi_i^\alpha \psi_j^\beta, \quad \langle \psi_{k,l}^\gamma \mid \psi_{k',l'}^{\gamma'} \rangle = \delta_{\gamma\gamma'} \delta_{kk'} \delta_{ll'} . \quad (3.2)$$

Tables I–III are concerned with the direct product between a single-group representation (Γ^α) and $D_{1/2}$ (Γ^β), which decomposes into some double-group representations (Γ^γ). In the case of Tables V–XI, Γ^α is an irreducible representation of $G_{\vec{k}}$ according to which the radiation operator transforms, while Γ^β and Γ^γ are some single- or double-group representations. Except for $D_{1/2}$ and the radiation operator representations, all other irreducible representations occurring in (3.1) have Bloch functions as basis functions. This means that $\Gamma(\{R \mid \vec{\tau} + \vec{f}_R\}) = e^{i\vec{k}\cdot\vec{\tau}} \Gamma(\{R \mid \vec{f}_R\})$ and therefore in (3.1) the phase factors $e^{i\vec{k}\cdot\vec{\tau}}$ associated with primitive translations cancel. For this reason the summation in (3.1) may be limited to those elements which have the form $\{R \mid \vec{f}_R\}$, i.e., the primitive translations may be neglected for the purpose of calculating Clebsch-Gordan coefficients and dipole-selection rules.

As a consequence of the introduction of the spin, the number of symmetry elements of the space group is doubled: a new element, obtained by multiplication with the rotation by 2π, must be added to every element of the space group, and the so-called double group is formed. A rotation by 2π in spin space is not the identity operation E: While in single-group representation it is represented by E, in double-group representations it is $-E$. However, since double-group representations occur always twice in (3.1), the new elements must not be taken into account for calculating Clebsch-Gordan coefficients.

For constructing the matrix (3.1) it is useful to treat separately (i) the points inside the Brillouin zone and (ii) the points on the surface.

(i) For $\vec{k}$ inside the Brillouin zone[11] $\Gamma(\{R \mid \vec{f}_R\}) = e^{i\vec{k}\cdot\vec{f}_R} \Gamma(\{R \mid \vec{0}\})$. Again we have the convenient property that the factor $e^{i\vec{k}\cdot\vec{f}_R}$ cancels, and the matrix representations of $\{R \mid \vec{0}\}$ suffice to construct the matrix (3.1). In this case the point-group Clebsch-Gordan coefficients apply to space groups, too.

(ii) For points and lines on the surface of the Brillouin zone the matrix representations are given by Slater[12] for many space groups, including O_h^7. As apparent from the comparison between the tables for the symmorphic space group O_h^5 ($Fm3m$, fcc lattices) and O_h^7, the use of point-group tables at the symmetry points L, U, and K, and the lines Q and S is justified. For the remaining symmetry points X and W and line Z the calculation must be made explicitly. Since the double-group representations are not supplied by Ref. 11, we must construct them in order to give the required tables. X_5 is constructed from $X_1 \otimes D_{1/2}$, with the matrices of $D_{1/2}$ also taken from Ref. 11. The one-dimensional representations at line Z and symmetry point W are easily obtained from the character tables given by Elliott.[6] The two-dimensional representation W_7 has been constructed using a standard method of calculation: From the characters of W_7, the appropriate basis ψ_1^7, ψ_2^7 in the space spanned by $W_1 \otimes D_{1/2}$ is derived by means of a projection-operator technique.[13] A suitable matrix representation for W_7 is then given by

$$\Gamma_{ij}^7 = \langle \psi_i^7 \mid W_1 \otimes D_{1/2} \mid \psi_j^7 \rangle, \; i,j = 1,2 .$$

TABLE X. Clebsch-Gordan coefficients for the decomposition of the direct product between the radiation representation Z_3^r and single- or double-group representations. Notation as in Tables I–III.

$Z_3^r \otimes Z_1$ $= Z_1$	$u_z v_1$	$u_z v_2$	$Z_3^r \otimes Z_k$ $(k=2,3,4,5)$	
ψ_1	0	1		i
ψ_2	1	0		

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[9]This is a special case of the Wigner-Eckart theorem for space groups, since in general the matrix elements are not proportional to a single known Clebsch-Gordan coefficient but are equal instead to a *sum* of known Clebsch-Gordan coefficients. It is at this point that there is a difference between the space groups and the full rotation group. However, this simplified version is the most commonly encountered.

[10]J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1965), Vol. 2, Appendix 3, Formula A3-4.

[11]J. C. Slater, Rev. Mod. Phys. 37, 68 (1965).

[12]See J. C. Slater, *Quantum Theory of Molecules and Solids,* Ref. 10, Appendix 3. There is an error on p. 383, Table A3-28: R_{15} and R_{16} must be interchanged at the top of the table to fulfill the (correct) multiplication table of the group, displayed in Table A3-17.

[13]See J. F. Cornwell, in *Group Theory and Electronic Energy Bands in Solids,* Ref. 7, p. 57.