# Light-induced electron-spin polarization in cubic crystals

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From general wave functions transforming irreducibly according to the double groups, generalized selection rules for the production of spin-polarized electrons in cubic crystals by circularly polarized light are derived. Nonzero results are obtained for the $\Delta$ and $\Lambda$ direction, with equal strength for spin-up and spin-down electrons of a particular transition, if right-circular polarization is changed to left-circular polarization. The strength depends on a parameter proportional to the integral performed on the spatial parts of the wave functions. The results can be easily applied to hybridization effects and are confirmed by recent experimental data on tungsten.

## I. INTRODUCTION

Photoemission of spin-polarized electrons induced by circularly polarized light may serve as an experimental method to obtain information on the electronic structure of solids.[1] The excitation of unpolarized electrons into spin-polarized final states is governed by selection rules which allow quite general predictions on the spin polarization to be made once the symmetries of the different electronic states are known. Such selection rules in the past have been derived by Koyama and Merz[2] and more recently by Reyes and Helman,[3] but their treatment of the problem does not exhaust all the information which may be gained from group-theoretical methods. Especially the question of how to take into account hybridization effects has not been answered and this deficiency resulted in severe discrepancies between theoretical predictions[3] and experimental results.[1] It is therefore the aim of this contribution to deduce those selection rules on a very general level which allow hybridization to be taken into account in an easy way.

## II. THEORY

The number of spin-polarized electrons, excited with circularly polarized light in unpolarized metals depends on the spin-orbit interaction and general symmetry requirements. Therefore general selection rules and the relative strength of different transitions can be calculated without an explicit consideration of the radial part of the wave functions involved.

In the presence of spin-orbit interaction, the symmetry properties of the electron-energy-band wave functions $\psi_{\vec{k}}(\vec{r})$ are described by the irreducible representations of the double group corresponding to the group of the wave vector $\vec{k}$.[4] These functions are composed of a spatial and a spin part. The spatial part of the wave function transforms according to one of the representations of the corresponding single group. Proper linear combinations of spatial and spin-wave functions can be easily constructed with the help of coupling coefficients given by Koster *et al.*[5]

We now restrict our calculation to spin-polarized electrons due to direct interband transitions induced by circularly polarized light along the [100] direction ($C_{4v}$ symmetry) and [111] direction ($C_{3v}$ symmetry) in cubic crystals. For the $\Delta$ direction ($C_{4v}$) we have four one-dimensional single-valued representations and one two-dimensional representation for possible spatial parts of the wave functions, while for $\Lambda(C_{3v})$ there are two one-dimensional representations and one two-dimensional one. The effect of spin-orbit coupling is introduced by multiplication of the single-group representations with the spin representations $(\Delta_6, \Lambda_6)$.

The reduction of these products yields for $C_{4v}$ and $C_{3v}$ symmetries:

$$\Delta_1 \times \Delta_6 = \Delta_6^1;\ \Delta_{1'} \times \Delta_6 = \Delta_6^{1'};\ \Delta_2 \times \Delta_6 = \Delta_7^2;\ \Delta_{2'} \times \Delta_6 = \Delta_7^{2'};\ \Delta_5 \times \Delta_6 = \Delta_6^5 + \Delta_7^5\ , \tag{1a}$$

$$\Lambda_1 \times \Lambda_6 = \Lambda_6^1;\ \Lambda_2 \times \Lambda_6 = \Lambda_6^2;\ \Lambda_3 \times \Lambda_6 = \Lambda_6^3 + \Lambda_4^3\Lambda_5^3\ . \tag{1b}$$

The representations are labeled according to Cornwell,[6] the subscript indicates the double group representation, the superscript the single-group representation from which it is derived; the $\Lambda_4^3\Lambda_5^3$ representations are taken together, because they are degenerate due to time-reversal symmetry.

We now present general symmetry-adapted functions. The spinors $\{|\alpha\rangle, |\beta\rangle\}$ with $|\alpha\rangle = |\uparrow\rangle$ and $|\beta\rangle = |\downarrow\rangle$ generate the representations $\Delta_6(\Lambda_6)$. The following functions define the spatial parts by specify-

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ing their transformation properties under $C_{4v}(C_{3v})$:

$$\begin{aligned}
&\Delta_1\text{: } w_1 \text{ transforms as } z \ , \\
&\Delta_2\text{: } w_2 \text{ transforms as } (x^2-y^2) \ , \\
&\Delta_{2'}\text{: } w_{2'} \text{ transforms as } x\cdot y \ , \\
&\Delta_5\text{: } \{v_x, v_y\} \text{ transforms as } \{s_x, s_y\} \ ,
\end{aligned} \tag{2a}$$

$$\begin{aligned}
&\Lambda_1\text{: } u_1 \text{ transforms as } z \ , \\
&\Lambda_2\text{: } u_2 \text{ transforms as } s_z \ , \\
&\Lambda_3\text{: } \{u_{-1}, u_{+1}\} \text{ transforms as } \{s_x - is_y, -(s_x + is_y)\} \ .
\end{aligned} \tag{2b}$$

Herein $x,y,z$ denote the components of a polar vector and $s_x, s_y, s_z$ those of an axial vector. The $z$ component is along $\Delta$ and $\Lambda$, respectively.

As shown above there are three types of $\Delta_6$ and $\Delta_7$ functions, while for the [111] direction three $\Lambda_6$ and one pair of $\Lambda_4\Lambda_5$ functions exist, each type being derived from a distinct single-valued representation. The corresponding basis functions follow from the tabulated coupling coefficients and are listed below, in a labeling scheme suggesting itself in the $C_{4v}$ and $C_{3v}$ symmetries:

$$\begin{aligned}
&\psi^1_{6,-1/2} = w_1|\beta\rangle; \qquad \psi^1_{6,1/2} = w_1|\alpha\rangle \ , \\
&\psi^2_{7,-1/2} = w_2|\beta\rangle; \qquad \psi^2_{7,1/2} = w_2|\alpha\rangle \ , \\
&\psi^{2'}_{7,-1/2} = iw_{2'}|\beta\rangle; \qquad \psi^{2'}_{7,1/2} = -iw_{2'}|\alpha\rangle \ , \\
&\psi^5_{6,-1/2} = \frac{1}{\sqrt{2}}(iv_x + v_y)|\alpha\rangle; \qquad \psi^5_{6,1/2} = \frac{1}{\sqrt{2}}(iv_x - v_y)|\beta\rangle \ , \\
&\psi^5_{7,-1/2} = \frac{1}{\sqrt{2}}(iv_x - v_y)|\alpha\rangle; \qquad \psi^5_{7,1/2} = \frac{1}{\sqrt{2}}(iv_x + v_y)|\beta\rangle \ ,
\end{aligned} \tag{3a}$$

$$\begin{aligned}
&\Phi^1_{6,-1/2} = u_1|\beta\rangle; \qquad \Phi^1_{6,1/2} = u_1|\alpha\rangle \ , \\
&\Phi^2_{6,-1/2} = iu_2|\beta\rangle; \qquad \Phi^2_{6,1/2} = -iu_2|\alpha\rangle \ , \\
&\Phi^3_4 = \frac{1}{\sqrt{2}}(u_{-1}|\beta\rangle - iu_{+1}|\alpha\rangle); \qquad \Phi^3_5 = \frac{1}{\sqrt{2}}(iu_{-1}|\beta\rangle - u_{+1}|\alpha\rangle) \ , \\
&\Phi^3_{6,-1/2} = u_{-1}|\alpha\rangle; \qquad \Phi^3_{6,1/2} = -u_{+1}|\beta\rangle \ .
\end{aligned} \tag{3b}$$

It should be noted, that we omitted wave functions transforming as $\Delta_{1'} \times \Delta_6$. This is not due to a group-theoretical argument, but, for reasons resting on the practice of band-structure calculations. In the Appendix A we have tabulated the angular parts of $s,p,d,f$ functions (spherical harmonics) transforming like the basis functions of the single-valued representations. As an interesting result no linear combination of spherical harmonics with $\mathfrak{L} \leq 3$ transforms as $\Delta_{1'}$ under $C_{4v}$.

Therefore for electric-dipole transitions with $\Delta\mathfrak{L} = \pm 1$ no transitions from or to a $\Delta_{1'}$ level can occur for $\mathfrak{L} < 4$. On the other hand, for example, in the Green's-function method spherical harmonics with $\mathfrak{L} \geq 4$ can be omitted without serious loss of accuracy.[7]

We now consider a transition of the system from state $\chi^{(i)}_\nu$ to the state $\chi^{(j)}_{\nu'}$, induced by the electric vector of incident light. The transition matrix element is

$$M^{i\rightarrow j}_{\nu'\nu} = \langle \chi^{(j)}_{\nu'} | \hat{\epsilon}\cdot\vec{Q} | \chi^{(i)}_\nu \rangle \ , \tag{4}$$

where $\hat{\epsilon}$ describes the polarization of the incident light and $\vec{Q}$ is the electric-dipole-moment operator. The wave functions belong to the representation $\Delta_i$ and $\Delta_j$, while the operator $\hat{\epsilon}\cdot\vec{Q}$ may belong to $\Delta_k$. Then $M^{i\rightarrow j}_{\nu'\nu}$ is zero unless $\Delta_k \times \Delta_i$ contains $\Delta_j$. Thus, knowing the transformation properties of the operator, we can deduce the selection rules for circularly polarized light, because such nonzero matrix elements have to be assumed to produce spin-polarized electrons.

The operators $Q_x - iQ_y$ with $\hat{\epsilon}_- = (1/\sqrt{2})(\hat{x} - i\hat{y})$ and $Q_x + iQ_y$ with $\hat{\epsilon}_+ = (1/\sqrt{2})(\hat{x} + i\hat{y})$ correspond to right-(left-) circularly polarized light propagating in the $-z$ direction. They both transform as $\Delta_5$ and $\Lambda_3$, respectively. The reduction of the products restricted

to the single group results in necessary conditions for nonzero matrix elements:

$$\begin{aligned}
&\Delta_5 \times \Delta_1 = \Delta_5 \rightarrow M^{1\rightarrow 5} \neq 0 \ , \\
&\Delta_5 \times \Delta_2 = \Delta_5 \rightarrow M^{2\rightarrow 5} \neq 0 \ , \\
&\Delta_5 \times \Delta_{2'} = \Delta_5 \rightarrow M^{2'\rightarrow 5} \neq 0 \ , \\
&\Delta_5 \times \Delta_5 = \Delta_1 + \Delta_{1'} + \Delta_2 + \Delta_{2'} \rightarrow M^{5\rightarrow 1} \neq 0; \ M^{5\rightarrow 2} \neq 0; \ M^{5\rightarrow 2'} \neq 0 \ ,
\end{aligned} \tag{5a}$$

$$\begin{aligned}
&\Lambda_3 \times \Lambda_1 = \Lambda_3 \rightarrow M^{1\rightarrow 3} \neq 0 \ , \\
&\Lambda_3 \times \Lambda_2 = \Lambda_3 \rightarrow M^{2\rightarrow 3} \neq 0 \ , \\
&\Lambda_3 \times \Lambda_3 = \Lambda_1 + \Lambda_2 + \Lambda_3 \rightarrow M^{3\rightarrow 1} \neq 0; \ M^{3\rightarrow 2} \neq 0; \ M^{3\rightarrow 3} \neq 0 \ .
\end{aligned} \tag{5b}$$

For the $\Delta$ direction we can expect spin-polarized electrons due to transitions between the doubly-degenerate state $\Delta_5$ and $\Delta_1,\Delta_2$ or $\Delta_{2'}$ and vice versa, while for the $\Lambda$ direction those between $\Lambda_3$ and $\Lambda_1,\Lambda_2,\Lambda_3$ can occur.

From this it is obvious that the condition of $Q_x$ and $Q_y$ belonging to the same irreducible representation requires a principal axis of an order higher than 2. This serves as a necessary condition for a nonzero spin polarization. In order to calculate the matrix elements $M^{i\rightarrow j}_{\nu'\nu}$ and the resulting electron-spin polarization we make use of the "generalized Wigner-Eckart theorem" developed by Koster[8]: The matrix elements $\langle \psi^j_{\nu'} | \vec{Q}_\mu | \psi^i_\nu \rangle$ and $\langle \Phi^j_{\nu'} | \vec{Q}_\mu | \Phi^i_\nu \rangle$ with $\mu = x,y$ are equal to a known matrix times a constant independent of $\nu$, $\nu'$, and $\mu$. To derive these matrices we remember that $\vec{Q}_\mu | \psi^5_\nu \rangle$ involves the spatial functions $\vec{Q}_\mu v_x$ and $\vec{Q}_\mu v_y$. The four functions are now projected with the help of the coupling coefficients onto the irreducible representations $\Delta_1,\Delta_2$ and $\Delta_{2'}$ of $C_{4v}$, because $Q_y$ transforms as $s_x$ and $-Q_x$ as $s_y$ of $\Delta_5$:

$$\begin{aligned}
&\Delta_1\text{:} \ \ Q_y v_x - Q_x v_y = a_1 \ , \\
&\Delta_2\text{:} \ \ Q_y v_x + Q_x v_y = a_2 \ , \\
&\Delta_{2'}\text{:} \ \ Q_y v_y - Q_x v_x = a_{2'} \ .
\end{aligned} \tag{6}$$

Let us consider the transition $\Delta^5_6 \rightarrow \Delta^1_6$, described by $\langle \psi^1_{6,\lambda'} | \vec{Q} | \psi^5_{6\lambda} \rangle$ with $\lambda, \lambda' = \pm \frac{1}{2}$. The spatial part of $\psi^1_{6,\lambda'}$ is $w_1$ and belongs to $\Delta_1$. This forms a nonzero scalar product with $a_1$ only. Therefore, the nonvanishing matrix elements are those proportional to

$$\langle w_1 | Q_y | v_x \rangle = - \langle w_1 | Q_x | v_y \rangle \ .$$

With this result in mind it is easy to calculate the desired matrix. For example,

$$\begin{aligned}
\langle \psi^1_{6,-1/2} | \vec{Q}_\mu | \psi^5_{6,1/2} \rangle &= \frac{1}{\sqrt{2}} \langle w_1 | \vec{Q}_\mu | i v_x + v_y \rangle \langle \beta | \beta \rangle \\
&= \tfrac{1}{2} ( i \vec{Q}_y - \vec{Q}_x ) \langle w_1 | Q_y | v_x \rangle \langle \beta | \beta \rangle \ .
\end{aligned}$$

We obtain

$$\langle \psi^1_{6,\lambda'} | \hat{\epsilon} \cdot \vec{Q} | \psi^5_{6,\lambda} \rangle = d^1_0 \begin{pmatrix} 0 & \epsilon_-(\beta) \\ -\epsilon_+(\alpha) & 0 \end{pmatrix} \ , \tag{6a}$$

where $2d^1_0 = \langle w_1 | Q_y | v_x \rangle$ and $\epsilon_+(\alpha)$ means that left-circularly polarized light produces $\alpha$ electrons. The parameter $d^1_0$ can be further reduced to a radial part only using the angular parts of the wave functions given in the Appendix A, or completely if wave functions from band-structure calculations are available.

In a similar way we obtain

$$\langle \psi^1_{6,\lambda'} | \hat{\epsilon} \cdot \vec{Q} | \psi^5_{7,\lambda} \rangle = d^1_0 \begin{pmatrix} 0 & \epsilon_+(\beta) \\ -\epsilon_-(\alpha) & 0 \end{pmatrix} \ . \tag{6b}$$

The remaining transition matrix elements follow in a straightforward manner from the fact that the spatial part of $\psi^2_{7,\lambda'}$ is $w_2$ and belongs to $\Delta_{2'}$ thus forming nonzero matrix elements which are proportional to $\langle w_2 | Q_y | v_x \rangle = \langle w_2 | Q_x | v_y \rangle$. It is found

$$\langle \psi^2_{7,\lambda'} | \hat{\epsilon} \cdot \vec{Q} | \psi^5_{6,\lambda} \rangle = d^2_0 \begin{pmatrix} 0 & -\epsilon_+(\beta) \\ +\epsilon_-(\alpha) & 0 \end{pmatrix} \ , \tag{6c}$$

$$\langle \psi^2_{7,\lambda'} | \hat{\epsilon} \cdot \vec{Q} | \psi^5_{7,\lambda} \rangle = d^2_0 \begin{pmatrix} 0 & +\epsilon_-(\beta) \\ -\epsilon_+(\alpha) & 0 \end{pmatrix} \ , \tag{6d}$$

where $2d_0^{2} = \langle w_z|Q_x|v_y\rangle$. Finally we obtain

$$\langle \psi^{2'}_{7,\lambda'}|\hat{\epsilon}\cdot\vec{Q}|\psi^{5}_{6,\lambda}\rangle = d_0^{2'}\begin{pmatrix} 0 & -\epsilon_+(\beta) \\ \epsilon_-(\alpha) & 0 \end{pmatrix} , \quad (6e)$$

$$\langle \psi^{2'}_{7,\lambda'}|\hat{\epsilon}\cdot\vec{Q}|\psi^{5}_{7,\lambda}\rangle = d_0^{2'}\begin{pmatrix} 0 & -\epsilon_-(\beta) \\ +\epsilon_+(\alpha) & 0 \end{pmatrix} , \quad (6f)$$

where $2d_0^{2'} = \langle w_{2'}|Q_x|v_x\rangle$.

The results are as follows:

(i) Spin polarization produced by left- and right-circularly polarized light have the same magnitude, but opposite sign.

(ii) Equivalent transitions between initial states of a distinct spatial part and those of final states with the same spatial part are equal in magnitude and produce the same sort of electrons but with different polarization of the light.

(iii) The relative strength of transitions to different spatial parts of the final state are proportional to $d_0^{1}:d_0^{2}:d_0^{2'}$.

For convenience the results are tabulated in Table I. This general result is in agreement with calculation of Reyes *et al.*,[3] derived from special wave functions.

The same arguments can be applied to the case of the $\Lambda$ direction. $x \mp iy$ transform as $\pm s_x - is_y$ of $\Lambda_3$ and $\vec{Q}|\Phi^3_\nu\rangle$ can be projected onto

$$\Lambda_1:\ Q_+u_{-1} + Q_-u_{+1} = b_1 ,$$
$$\Lambda_2:\ Q_-u_{+1} - Q_+u_{-1} = b_2 , \quad (7)$$
$$\Lambda_3:\ Q_+u_{+1} = b^3_{-1},\ \ Q_-u_{-1} = b^3_{+1},\ \text{with } Q_\pm = Q_x \pm iQ_y .$$

This yields the following matrices for the transitions of interest

$$\langle \Phi^{1}_{6,\lambda'}|\hat{\epsilon}\cdot\vec{Q}|\Phi^3_4\Phi^3_5\rangle = f_0^{1}\begin{pmatrix} \epsilon_+(\beta) & i\epsilon_+(\beta) \\ -i\epsilon_-(\alpha) & -\epsilon_-(\alpha) \end{pmatrix} , \quad (7a)$$

with $f_0^{1} = \langle u_1|Q_-|u_{+1}\rangle$,

$$\langle \Phi^{1}_{6,\lambda'}|\hat{\epsilon}\cdot\vec{Q}|\Phi^3_{6,\lambda}\rangle = f_0^{1}\begin{pmatrix} 0 & -\sqrt{2}\epsilon_-(\beta) \\ \sqrt{2}\epsilon_+(\alpha) & 0 \end{pmatrix} , \quad (7b)$$

$$\langle \Phi^{2}_{6,\lambda'}|\hat{\epsilon}\cdot\vec{Q}|\Phi^3_{6,\lambda}\rangle = f_0^{2}\begin{pmatrix} 0 & -i\sqrt{2}\epsilon_-(\beta) \\ i\sqrt{2}\epsilon_+(\alpha) & 0 \end{pmatrix} , \quad (7c)$$

with $f_0^{2} = \langle u_2|Q_-|u_{+1}\rangle$,

$$\langle \Phi^{2}_{6,\lambda'}|\hat{\epsilon}\cdot\vec{Q}|\Phi^3_4\Phi^3_5\rangle = f_0^{2}\begin{pmatrix} i\epsilon_+(\beta) & \epsilon_+(\beta) \\ -\epsilon_-(\alpha) & i\epsilon_-(\alpha) \end{pmatrix} , \quad (7d)$$

$$\langle \Phi^3_4\Phi^3_5|\hat{\epsilon}\cdot\vec{Q}|\Phi^3_4\Phi^3_5\rangle = \langle \Phi^{3}_{6,\lambda'}|\vec{Q}|\Phi^3_{6,\lambda}\rangle = 0 , \quad (7e)$$

$$\langle \Phi^3_4\Phi^3_5|\hat{\epsilon}\cdot\vec{Q}|\Phi^{3}_{6,\lambda}\rangle = f_0^{3}\begin{pmatrix} -i\epsilon_-(\alpha) & -\epsilon_+(\beta) \\ -\epsilon_-(\alpha) & i\epsilon_+(\beta) \end{pmatrix} , \quad (7f)$$

with $f_0^{3} = \langle u_{-1}|Q_+|u_{+1}\rangle$. It is interesting to note, that the last transition in Eq. (7e) is allowed by general symmetry arguments but becomes accidently zero, because $u_{\pm 1}$ forms only nonzero matrix elements with $b^3_{\pm 1'}$ while the first one vanishes if the double group is applied. The last transitions $\langle \Phi^3_{\nu'}|\vec{Q}|\Phi^3_{6,\lambda}\rangle$ with $\nu' = 4, 5$ have not been considered by Reyes.[3] This is probably due to the fact that they calculated only one set of $d$ functions transforming as $\Lambda_{3'}$ while in general there is a second one as can be seen by inspection of the corresponding compatibility table. This additional set has been added in Appendix A. Since $f$ electrons are taken into account we get two further transitions $\Lambda^2_6 \rightarrow \Lambda^3_4\Lambda^3_5$ and $\Lambda^2_6 \rightarrow \Lambda^3_6$ producing spin-polarized electrons. Again our general statements (i)–(ii) are fulfilled, because the states $\Lambda^3_4\Lambda^3_5$ are degenerate due to time-reversal symmetry and have to be considered together. Table II collects the results obtained.

TABLE I. Electron-spin polarization for the $\Delta$ direction. Initial states are on the left, final ones on the top. The table shows the results for right-circularly polarized light; to obtain those for the opposite case $\alpha$ and $\beta$ have to be interchanged.

| | $\Delta^1_6$ | $\Delta^2_7$ | $\Delta^{2'}_7$ | $\Delta^5_6$ | $\Delta^5_7$ |
|---|---|---|---|---|---|
| $\Delta^1_6$ | . . . | . . . | . . . | $\alpha$ | $\beta$ |
| $\Delta^2_7$ | . . . | . . . | . . . | $\beta$ | $\alpha$ |
| $\Delta^{2'}_7$ | . . . | . . . | . . . | $\beta$ | $\alpha$ |
| $\Delta^5_6$ | $\beta$ | $\alpha$ | $\alpha$ | . . . | . . . |
| $\Delta^5_7$ | $\alpha$ | $\beta$ | $\beta$ | . . . | . . . |

TABLE II. Electron-spin polarization for the Λ direction. Notation as explained in Table I.

| | $\Lambda_6^1$ | $\Lambda_6^2$ | $\Lambda_4^3\Lambda_5^3$ | $\Lambda_6^3$ |
|---|---|---|---|---|
| $\Lambda_6^1$ | ... | ... | $\beta$ | $\alpha$ |
| $\Lambda_6^2$ | ... | ... | $\beta$ | $\alpha$ |
| $\Lambda_4^3\Lambda_5^3$ | $\alpha$ | $\alpha$ | ... | $\beta$ |
| $\Lambda_6^3$ | $\beta$ | $\beta$ | $\alpha$ | ... |

## III. HYBRIDIZATION EFFECTS AND APPLICATIONS

The very general calculation enables us to take into account hybridization easily. The most general forms of wave functions transforming like $\Delta_6$ or $\Delta_7$ are

$$\psi_{6,\lambda} = a_6\psi^1_{6,\lambda} + b_6\psi^5_{6,\lambda} \ , \tag{8}$$

(initial state),

$$\psi_{7,\lambda'} = a_7\psi^2_{7,\lambda'} + b_7\psi^{2'}_{7,\lambda'} + c_7\psi^5_{7,\lambda'} \ , \tag{9}$$

(final state), with $a_6, \ldots, c_7$ describing the degree of hybridization. Let us consider for example right-circular polarization, i.e., $\vec{Q}$ along $\hat{\epsilon}_-$. Then

$$\langle\psi_{7,\lambda'}|\hat{\epsilon}_-\cdot\vec{Q}|\psi_{6,\lambda}\rangle = (+a_7^* b_6 d_0^2 + b_7^* b_6 d_0^{2'})\epsilon_-(\alpha) + c_7^* a_6 d_0^{1*}\epsilon_-(\beta) \ . \tag{10}$$

From this it is obvious that in general an electron-spin polarization less than 100% must be expected, depending on the degree of hybridization. Further information can be extracted from a discussion of the parameter $d_0^\nu$ in Eq. (10). These parameters describe the radial and the angular part of an unknown matrix element between a $\Delta^5$ level and a $\Delta^\nu$ level, with $\nu = 1, 2, 2'$. From the table in Appendix A $d_0^2$ and $d_0^{2'}$ are determined to be zero if the initial level has $d$-band character and the final one is $p$-bandlike, because there are no $p$ functions transforming like $\Delta^2$ and $\Delta^{2'}$. Thus, if $\alpha$ electrons are observed, the transition should be of the type $p \rightarrow d$, provided $f$ functions may be neglected. The parameter $d_0^1$ is nonzero, except for a transition of the type $p \rightarrow s$, because no $s$ function transforming like $\Delta^5$ exists.

Finally we discuss in some detail the more complex situation of a $\Delta_7 \rightarrow \Delta_7$ transition. We have

$$\psi_{7,\lambda} = a_7\psi^2_{7,\lambda} + b_7\psi^{2'}_{7,\lambda} + c_7\psi^5_{7,\lambda} \ , \tag{11}$$

(initial state),

$$\psi_{7,\lambda'} = a_7'\psi^2_{7,\lambda'} + b_7'\psi^{2'}_{7,\lambda'} + c_7'\psi^5_{7,\lambda'} \ , \tag{12}$$

(final state), and therefore

$$\langle\psi_{7,\lambda'}|\hat{\epsilon}_-\cdot\vec{Q}|\psi_{7,\lambda}\rangle = (-c_7'^* a_7 d_0^{2*} + c_7'^* b_7 d_0^{2'*})\epsilon_-(\alpha) + (+a_7'^* c_7 d_0^2 - b_7'^* c_7 d_0^{2'})\epsilon_-(\beta) \ . \tag{13}$$

Neglecting $f$ functions we conclude in a similar way, that the production of spin-up electrons requires an initial state with $p$ character and a final one with $d$-wave function. Spin-down electrons are achieved by a $d$-type initial state and a final one with $p$ character. Consequently an electron-spin polarization less than 100% requires $p$-$d$ hybrids for both the initial and the final state of a $\Delta_7 \rightarrow \Delta_7$ transition, as long as $f$-wave functions are disregarded. For the case of the Λ direction similar results may be deduced.

Unfortunately, very few experimental results on electron-spin polarization in single crystals have been published. We therefore briefly comment on the electron-spin-polarization measurements on tungsten, recently presented by Zürcher *et al.*[1] With the help of our general results we may get an insight into several simplifications used in this paper to derive some quantitative results. According to this work two transitions labeled $T_1(\Delta_7 \rightarrow \Delta_7)$ and $T_2(\Delta_6 \rightarrow \Delta_7)$ contribute to the spectrum. Hybridization has to be taken into account for both transitions, because a spin polarization much lower than 100% was observed. For the $T_1$ transition $p$-$d$ hybrids are claimed which is in agreement with our general results deduced above. On the other hand, only two distinct spatial parts $(\Delta_7^{2'}, \Delta_7^5)$ have been taken into account for the $\Delta_7$ levels, while in general three contributions are expected, cf. Eqs. (11) and (12). From the band-structure calculation used by those authors a contribution of the $\Delta_7^2$ level smaller than that of the $\Delta_7^{2'}$ and $\Delta_7^5$ levels seems reasonable. But a zero one seems doubtful, since on the other hand for the $T_2$ transition a hybridization of $\Delta_6^5$ with $\Delta_{6'}^1$ which is at least equally separated in energy, must be introduced to explain the observed spin polarization. As simple relations between the coefficients $b_7, c_7, b_7', c_7'$ do not

TABLE III. Spatial parts of the wave functions transforming irreducibly under $C_{4v}$ and $C_{3v}$.

| Representations | Spherical harmonics | |
|---|---|---|
| | $C_{4v}$ symmetry | |
| $\Delta_1$ | $Y_l^0$, | $0 \leq l \leq 3$ |
| $\Delta_2$ | $\frac{1}{\sqrt{2}}(Y_l^2 + Y_l^{-2})$, | $2 \leq l \leq 3$ |
| $\Delta_{2'}$ | $-\frac{i}{\sqrt{2}}(Y_l^2 - Y_l^{-2})$, | $2 \leq l \leq 3$ |
| $\Delta_5$ | $\{\frac{i}{\sqrt{2}}(Y_l^1 + Y_l^{-1}), \frac{1}{\sqrt{2}}(Y_l^1 - Y_l^{-1})\}$ | $1 \leq l \leq 3$ |
| | $\{\frac{i}{\sqrt{2}}(Y_3^3 + Y_3^{-3}), -\frac{1}{\sqrt{2}}(Y_3^3 - Y_3^{-3})\}$ | |
| | $C_{3v}$ symmetry | |
| $\Lambda_1$ | $Y_2^0$, $0 \leq l \leq 3$; $\frac{1}{\sqrt{2}}(Y_3^3 - Y_3^{-3})$ | |
| $\Lambda_2$ | $-\frac{i}{\sqrt{2}}(Y_3^3 + Y_3^{-3})$ | |
| $\Lambda_3$ | $\{Y_l^{-1}, -Y_l^1\}$, | $1 \leq l \leq 3$ |
| | $\{Y_l^2, Y_l^{-2}\}$, | $2 \leq l \leq 3$ |

exist, it is felt that a quantitative interpretation of the $T_1$ transition requires more detailed information on the band structure of tungsten, calculations of which are in progress. Similar remarks apply for the $T_2$ transition, because it has the same final-state symmetry as $T_1$.

## IV. CONCLUSION

Starting with general wave functions transforming irreducibly according to the double groups of $C_{4v}$ and $C_{3v}$ we calculated generalized selection rules for the production of spin-polarized electrons in cubic crystals by circularly polarized light. Nonzero results are obtained for the $\Delta$ and $\Lambda$ direction, with equal strength for spin-up and spin-down electrons of a particular transition, if right-circular polarization is changed to left-circular polarization. The strength depends on a parameter proportional to the integral performed on the spatial part of the wave function. The results can be easily applied to hybridization effects, responsible for electron-spin polarization less than 100%. In addition predictions on hybrids are made and are confirmed by experimental results on tungsten.

## APPENDIX A

Here we present the spatial parts of the wave functions transforming irreducibly under $C_{4v}$ and $C_{3v}$ as defined by Koster *et al.*[5] The functions are normalized and given in the phase convention of Condon and Shortley (see Table III).

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