

PARTIAL PROBABILITIES OF X-RAY BREMSSTRAHLUNG TRANSITIONS

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High-energy electrons bombarding a solid produce X-ray bremsstrahlung radiation, which is one of few elementary processes occurring during electron–solid interactions. Photon emission results from electron transition to an unoccupied electron state above the Fermi level. In this work matrix elements of X-ray bremsstrahlung transitions were calculated for solids containing elements from N ($Z = 7$) to Pd ($Z = 46$) and photon energies 1487 eV and 5415 eV. It was found that in the case of light elements the X-ray bremsstrahlung transitions to s -type final states dominate over all other symmetries. It was also shown that X-ray bremsstrahlung transition probabilities increase with decreasing photon energy and increasing atomic number Z . Dependence of X-ray bremsstrahlung transition probabilities on the electron final state energy is also presented in this work.

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X-ray bremsstrahlung radiation is emitted during electron deceleration in a solid. It accompanies electron transitions from high energy states to low energy states above the Fermi level. Bremsstrahlung isochromat spectroscopy (BIS) allows us to probe the density of unoccupied electron states in a solid. The BIS method in contrary to extended X-ray absorption fine structure (EXAFS) is not unambiguously chemically specific, however, BIS cross-sections still depend on the atomic number Z and, above all, on the transition energy.

In BIS theory developed by Šimůnek et al. [1–3] the initial state of the electron is represented by a plane wave plus an outgoing spherical wave, while the final state is represented by a plane wave plus an incoming spherical wave. Any electron wave function can be decomposed into a sum of partial waves. According to the dipole approximation for X-ray bremsstrahlung transitions, a final electron state with symmetry l can be reached only from initial electron states having symmetries $l' = l + 1$ or $l' = l - 1$.

The intensity of X-ray bremsstrahlung radiation can be expressed as a sum of partial densities of states n_l , weighted by partial probabilities of bremsstrahlung transition to the final state with symmetry l (denoted by σ_l)

$$I \propto \sum_l \sigma_l n_l. \quad (1)$$

The aim of this work is to answer the questions, which symmetries of final states affect strongly bremsstrahlung isochromat intensity and which transitions are negligible in case of different elements, different photon energies and different energies of final states.

Since 1977 BIS transition probabilities could be roughly estimated from cross-sections for the direct radiative capture of electrons by stripped ionic targets using the effective-charge approximation and the scaling property proposed by Hahn and Rule [4]. In 1988 transition probabilities for few elements of $3d$ and $4d$ transition metals at the photon energies 1487 and 5415 eV were calculated and published [1, 5]. No data on BIS transition probabilities for light elements like oxygen, nitrogen and silicon have been published till present.

In this work we calculated for the first time the partial probabilities of X-ray bremsstrahlung transitions for light elements and compare them with those calculated for some $3d$ and $4d$ transition metals. We performed our calculations for solid crystalline silicon and its compounds, SiO_2 and Si_3N_4 , and for Al, Ti, V, Mn, Cu, Y, Pd metals. We chose two photon energies, 1487 and 5415 eV, which were mostly used in BIS experiments. We also show in this work to what extent does the chemical environment of the central atom influence the bremsstrahlung transition probabilities.

Self-consistent muffin-tin potentials of Moruzzi *et al.* [6] were used in our calculations for metals (note that no significant differences appear between bremsstrahlung transition probabilities obtained from self-consistent and non-self-consistent potentials for Cu [3]). For compounds containing Si, O and N (i.e. crystalline Si, β -quartz [7] and α - Si_3N_4 [8]) atomic electron densities were calculated self-consistently and the non-self-consistent muffin-tin potential was constructed via the Mattheiss [9] procedure.

Radial parts of matrix elements for bremsstrahlung transitions were calculated using a method previously described in [1] and developed in [2, 10]. Both initial and final electron states are treated as unbounded and delocalized. Matrix element is defined as

$$M_{fi} = \int \psi_f^* H_{\text{int}} \psi_i d\tau, \quad (2)$$

where H_{int} describes the interaction of the electron with the radiation field.

Radial part of matrix element in the dipole approximation can be written as

$$q_{l,l'} = \int r^2 dr R_{k,l}^0(r) r R_{k',l'}(r), \quad (3)$$

where $R_{k',l'}$ is a radial part of initial electron wave function and $R_{k,l}^0$ is a radial part of final electron wave function. Both radial functions are solutions of the Schrödinger equation for electron having momentum k and angular momentum

characterised by a quantum number l . The energy of the emitted bremsstrahlung photon ("isochromat energy") is

$$\hbar\omega = \frac{\hbar^2 k'^2}{2m} - \frac{\hbar^2 k^2}{2m}. \quad (4)$$

We calculated radial parts of matrix elements for the chosen elements and for two isochromat energies. Transitions to states having symmetries $l = 0, 1, 2$ (s, p, d) were taken into consideration (transitions to f -states were found to be negligible). Our calculations were performed for final energy range up to 250 eV above muffin-tin zero.

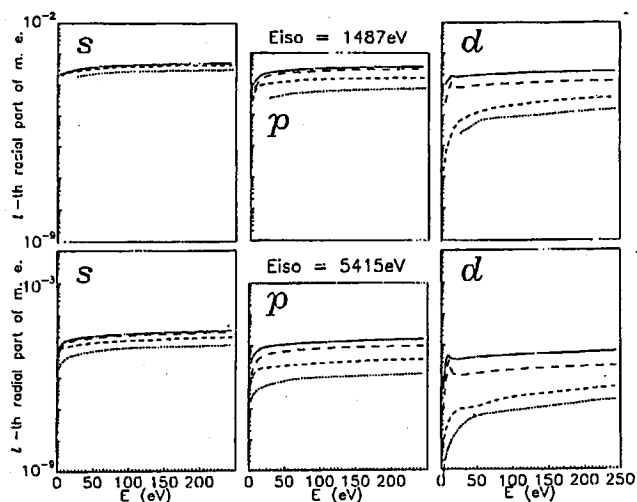


Fig. 1. Radial matrix elements $q_{l,l+1}$ for descending transitions to s -, p - and d -states calculated as a function of final state energy E for two isochromat energies 1487 eV and 5415 eV. Data for N (short dashes), Al (medium dashes), Mn (long dashes) and Y (solid line) are presented.

Figure 1 shows radial parts of matrix elements $q_{l,l'}$ for some of the considered elements as a function of final-state energy and for two considered isochromat energies. Zero point on the energy scale corresponds to the muffin-tin zero. Fermi level is usually few electron volts above muffin-tin zero [6]. Radial parts of matrix elements associated with ascending transitions ($l' = l - 1$) are 10 times lower than those associated with descending transitions ($l' = l + 1$). Therefore they are not presented in Fig. 1.

We have found $q_{l,l'}$ increasing together with the atomic number Z . For a given element, it is lower for transitions to states having higher l and it can be considered nearly zero for $l > 2$. A strong dependence of radial part of matrix elements on isochromat energy $\hbar\omega$ was observed: they decrease by order of magnitude with increasing photon energy from 1487 eV to 5415 eV. Radial parts of matrix elements depend on the energy of the final state E ; a rapid increase can

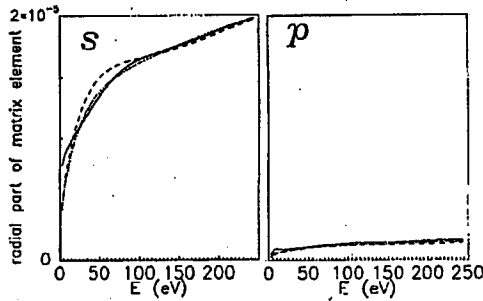


Fig. 2. Influence of chemical environment on radial parts of matrix elements associated with descending transition to s - and p -states for Si (for 5415 eV isochromat energy). Values of $q_{l,l+1}$ as a function of final state energy E are shown for Si in Si_3N_4 (short dashes), Si in SiO_2 (long dashes) and crystalline Si (solid line).

be seen for energies close to Fermi level and almost energy independent behaviour for final energies above 25 eV (see Fig. 1). We have noticed that the quotient $q_{l,l'}/\sum_{l,l'} q_{l,l'}$ remains nearly constant within the whole considered range of final energy.

Radial parts of matrix elements calculated for different chemical environment of the Si atom are shown in Fig. 2. The figure presents slightly different values of radial matrix elements for Si atoms in oxide, nitride and crystalline Si calculated for considered final energy range. The deviation caused by chemical environment of Si atoms is smaller than the difference between values of radial parts of matrix element calculated for Si ($Z = 14$) and Al ($Z = 13$).

Partial probability of bremsstrahlung transition entering Eq. (1) can be expressed by the following formula [10]:

$$\sigma_l = \frac{2\pi f^2}{\hbar^4 k'^2 [s_l^2(k)]} \sum_{l',l''} i^{l'-l''} \exp[i\delta_{l'}(k')] \exp[-i\delta_{l''}(k')] q_{l,l'} q_{l,l''} p_{l,l',l''}(\zeta), \quad (5)$$

where $p_{l,l',l''}(\zeta)$ is associated with angular part of matrix element and polarization of emitted photon, $s_l(k)$ and f are normalization factors. Partial probability of X-ray bremsstrahlung transition calculated from (5) depends on atomic number Z , transition energy $\hbar\omega$, angular momentum of final-state wave function l , final-state energy E , and the angle ζ between the electron and photon beams. We performed our calculations for the same parameters as in the case of radial parts of matrix elements and for $\zeta = 90^\circ$. Averaging over sample orientation was performed to keep the correspondence to amorphous or polycrystalline form of sample.

In Fig. 3 a quotient of $\sigma_l/\sum_l \sigma_l$ for transitions to final states $l = 0, 1, 2$ as a function of atomic number Z is shown with a solid line. It can be seen in the figure that for light elements the transition to s -states is dominant, while for heavier elements all three quotients associated with transitions to s -, p -, and d -states are comparable. In the case of the heaviest considered element (Pd, $Z = 46$), all quotients are almost equal to each other for $\hbar\omega = 1487$ eV, while for $\hbar\omega = 5415$ eV the s -like quotient is still the dominant one. Results shown in

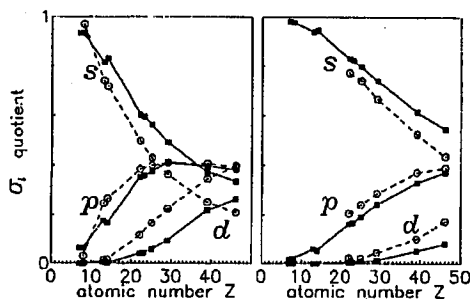


Fig. 3. Quotients $\sigma_l/(\sigma_0 + \sigma_1 + \sigma_2)$ for l -th radial parts of partial probabilities as a function of Z number calculated for transitions to final states having $l = 0, 1, 2$ and energy $E = 164$ eV. Results for free-free electron transitions in atoms are depicted by solid lines, results for free-bounded electron transitions in hydrogen-like atoms are shown with dashed lines.

Fig. 3 were obtained for final-state energy $E = 164$ eV, but they are very similar for the whole considered range of final energy.

We also calculated l -th partial probabilities as function of Z number in free-bounded electron transition approximation using tabulated cross-sections of electron capture in hydrogen-like atoms and scaling properties by Hahn and Rule [4]. A qualitative agreement between free-free and free-bounded partial transition probabilities calculations can be observed from the curves presented in Fig. 3. There is a critical insufficiency in Hahn and Rule's tabulated data for light elements and 5415 eV isochromat energy: the data cannot be obtained from the scaling procedure described in their work. It makes them unsuitable for interpretation of BIS spectra of light elements (up to $Z = 23$, i.e. vanadium). A small undervaluation of s -state contribution accompanied by overvaluation of p - and d -state contributions can be seen as a result of hydrogen-like atom treatment applied in the approach proposed by Hahn and Rule.

Concluding, we can say that the radial parts of matrix element increase monotonically together with atomic number Z . They are significantly larger for isochromat energy of 1487 eV than for the 5415 eV isochromat. For a fixed element and isochromat energy it was found that all partial radial parts of matrix elements as well as their quotients $q_{l,\nu}/\sum_{l,\nu} q_{l,\nu}$ are almost constant in the wide range of final electron energies. We found that only probabilities of transitions from p - to s - and from d - to p -states need to be taken into account in BIS investigations for light elements. Transitions from f - to d -states have to be enclosed into consideration for elements heavier than manganese ($Z = 25$). We also demonstrated that the influence of chemical environment on the magnitude of BIS matrix elements is almost negligibly small. Results obtained in the presented work enables BIS analysis of crystals and compounds containing light elements.

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