Selection rules and extended x-ray bremsstrahlung isochromat spectra of Cu and Pd

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We have calculated matrix elements for bremsstrahlung isochromat spectroscopy for the extended energy region 50–380 eV above the Fermi level. We have found that the transition rate depends on the atomic number, photon energy of the isochromat, and the angular momentum quantum number of the final-state wave function. The ratios of s, p, and d components of transition probability for the photon energies 1487 and 5415 eV are presented for Cu and Pd. We have demonstrated that the decelerated final electron originates in the core region of an atom, and we have explained why the main information to be gained from studying fine structure in the extended region of x-ray bremsstrahlung isochromat spectra is actually structural.

Bremsstrahlung isochromat spectroscopy (BIS) is an established technique for the study of the unoccupied electronic states of solids. Analysis of BIS data traditionally relies on the assumption that BIS gives a picture related to the total density of states (DOS) and is complementary to x-ray-absorption spectroscopy (XAS), which probes only the local and angular momentum l partial DOS. Indeed the strong parallels between the structure in the BIS spectra in the region up to ~70 eV above Fermi level E_F, measured at the isochromat photon energy of 1487 eV, and the calculated DOS were shown for Cu, Pd, and Ag metals by Speier et al.[1] Quite recently, however, Sobczak and Auleytner[2] (SA) measured BIS spectrum of Pd up to 130 eV above E_F for an isochromat photon energy of 5415 eV and found that their structure of the BIS spectrum differs from that of Ref. 1 and, at the same time, is strikingly similar to the p-like partial DOS calculated by Müller and Wilkins.[3] This result was interpreted by SA as being due to a specific energy dependence of the transition probability for different orbital angular momenta of the final electron state.

The dependence of transition-matrix elements in BIS on atomic number and angular momentum was recently computed for solid elements Al and the $3d$ and $4d$ series.[4] In these calculations, the energy of the isochromat was 1487 eV and only the low-energy region of final electronic states up to 26 eV was studied. Calculations of the transition-matrix element for higher-energy regions and for different energies of the isochromat do not exist. The need for quantitative evaluation of the BIS matrix element is now more pressing because the extended x-ray bremsstrahlung isochromat fine structure (EXBIFS) is used for the determination of interatomic distances in solids in the same way[2,5,6] as the extended x-ray-absorption fine structure (EXAFS).

In this work we have studied the dependence of transition probability on the angular quantum number for the two most common experimental energies of the iso-chromats, 1486.7 and 5415 eV, in the energy region up to 400 eV above E_F for Pd and Cu. Our aim is to explain experimental results[1,2] that give a quantitative description of BIS matrix element effect in the extended energy region, and to clarify the experimental evidence[2,5,6] that EXAFS and EXBIFS have the same origin and analogous descriptive equations.

Consider the high energy of the incident BIS electron of about 1.5 or 5.5 keV, and the final-electron energies in the energy range of 50–400 eV above E_F as the description of the transition; this allows us to split the calculation of the transition rate into two steps. The first step, which is atomic in character, consists of a deceleration of the incoming electron into the outgoing one; the second step, which is solid-state in character, modifies the outgoing electron due to scattering by the surrounding atoms. Taking into account the free-electron nature of the initial and final electrons, the initial wave function of an incident electron is asymptotically normalized to a unit amplitude plane wave of energy E_i and momentum P_i plus an outgoing spherical wave; the final wave function of an outgoing electron is asymptotically normalized to a unit amplitude plane wave of energy E_f and momentum p_f plus an incoming spherical wave. Both wave functions ψ_f, ψ_i can be written in the form

$$\psi_k(r) = \frac{1}{2k}\sum_{l=0}^{\infty} i^l(2l+1)e^{\pm i\delta_l}R_{kl}(r)P_l(\cos\theta), \quad (1)$$

where the radial wave functions of the initial and final states of the energies $E = \hbar^2 k^2/2m$ are exact solutions of the radial Schrödinger equation inside the muffin-tin potential adjusted to the spherical Bessel and Neumann function on the muffin-tin radius R_{MT} via the phase shift δ_l. The functions P_l are Legendre polynomials of argument $\cos\theta = \mathbf{k}\cdot\mathbf{r}/kr$.

The transition-matrix element M_{fi} between initial state ψ_i and final state ψ_f is for the atomiclike process in the

nonrelativistic approximation for radiative transitions

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

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

$$H_{int} \sim \epsilon \cdot p e^{-i q \cdot r} .\qquad (3)$$

ϵ and q are the photon polarization and wave vector q, respectively, $qc = \omega$. Because of the great energy difference $E_f - E_i = \hbar \omega$ oscillations in the wave function of the incoming electron have a much shorter period than the oscillations in the wave function of the decelerated outgoing electron. As a consequence, the major contribution to the matrix element comes from a distance[7] $\rho \sim \hbar / |p_f - p_i|$. For distances larger than ρ, the contribution is small because the wave functions oscillate rapidly in a region where r is practically constant; for smaller distances, $d\tau \sim r^2 dr$ is small. We may, therefore, consider the quantity ρ as the most important impact parameter. In the case of isochromat photon energies 1487 or 5415 eV and BIS extending 400 eV above E_F, ρ is in the interval of about 0.01–0.1 Å. Since the distance ρ is much smaller than the wavelength of the isochromats, the dipole approximation for H_{int} in (3) can be used. According to dipole selection rules the partial-l-transition-matrix element (2) can be evaluated for all l components of ψ_f in the l sum in (1). The fact that outgoing electron comes from the core region of the atom has crucial significance for the second step consisting in backscattering from near neighbors.

The initial and final radial wave functions $R_{kl}(r)$ in (1) of energies E_i and E_f were found by numerical integration of a radial Schrödinger equation. The self-consistent muffin-tin potentials of Pd and Cu (Ref. 8) were used. Since the region of the atom contributing the most to the matrix element is in the core of the atoms, where self-consistency and muffin-tin approximation only slightly change the original atomic potential, it can be expected that the potential of a neutral atom will provide very similar results. For the purpose of the quantitative estimate we performed the neutral and muffin-tin potential calcula-

tions only for Cu, where stronger differences could be anticipated than for Pd.

The partial matrix elements in the dipole approximations for the final states $l = 0,1,2,3$, i.e., s, p, d, and f functions R_{kl} in (1) were numerically integrated up to the point $R > R_{MT}$, then the phase-shifted free-field wave functions and the integration-by-parts methods were used. To obtain final atomic transition probability the squares of the partial matrix elements were multiplied by the corresponding angular factors to respect the most common experimental setup in which the direction of the emitted photons is perpendicular to the incoming electron beam.

The relative ratios of the partial transition probabilities for the final states with energies from 54.4 to 381 eV are presented in Table I. All ratios are related to the corresponding s-like probabilities which are by definition equal to 1 and therefore not given in Table I. The f-like probabilities are quite small and for this reason are not indicated.

These results show that the ratios of the partial transition probabilities strongly depend on the atomic number and photon energy of a particular isochromat. The s, p, d ratios for a fixed element and the photon energy changes slowly within the final-state energy range 55–380 eV. This nearly invariable mixture of the s, p, d final states in BIS is the cause of the similarities of BIS with the total DOS, partial DOS, or XAS. We also see that the mixture based on atomic potentials or solid-state muffin-tin potentials is practically the same, which proves the localized character of transition and the independence of ratios on the bonds in a solid. This fact makes it possible to utilize extended BIS for structural studies of solids.

The computed ratios together with partial and total DOS calculations[1,3] and calculated XAS of Cu (Ref. 9) and Pd (Ref. 3) explain the interpretations of Speier, Zeller, and Fuggle[1] and SA experiments. In the case of Cu, the breakdown of the total DOS into its different l components discloses a strong hybridization.[1] Consequently no significant effect in BIS in the region up to ~70 eV above E_F would occur if the matrix element for one component is exceptionally high.[1] It is also interesting to note that calculated K, L_1, L_2, and L_3 x-ray-

TABLE I. The relative $s:p:d$ ratios of the partial transition probabilities for the final states with the energies $E_f = 54.4$–380.9 eV are presented. All ratios are related to the corresponding s-like probability which is by definition equal to 1 and therefore not included in the table. The first three columns correspond to transition energy of 1486.6 eV, the last two columns to transition energy of 5415 eV. In the first column, Cu (at) denotes that atomic potential of Cu was used. The results in other columns are based on the self-consistent muffin-tin potentials of Moruzzi et al. (Ref. 8).

E_f (eV)		$\hbar\omega = 1486.6$ eV			$\hbar\omega = 5415$ eV	
		Cu(at)	Cu	Pd	Cu	Pd
54.4	p	3.21	3.47	4.48	1.46	2.75
	d	1.77	1.83	6.95	0.19	1.34
163.3	p	3.40	3.40	4.41	1.46	2.77
	d	1.80	1.76	6.38	0.20	1.31
272.2	p	3.32	3.30	4.34	1.46	2.74
	d	1.79	1.76	6.02	0.22	1.31
380.9	p	3.19	3.20	4.27	1.45	2.72
	d	1.77	1.77	5.77	0.24	1.31

absorption spectra up to ~220 eV have all significant features alike.[9]

The case of Pd is different than Cu. The observed BIS for a photon energy of 1487 eV strongly resembles the calculated total DOS (Ref. 1) because of fortuitous mixture of s, p, and d components.[4] However, for a photon energy of 5415 eV the mixture of the s, p, d components is very different from the former case. Here the contribution of the p-like component is highest which correlates p-like partial DOS and K XAS of Pd with BIS measured by SA.

The similarity of the experimental BIS and XAS in the extended energy region is strong but circumstantial evidence that EXAFS and EXBIFS have the same origin.[2,5] Actually existence of the fine structure in the extended BIS originates from the fact that the decelerated final electron in BIS arises in the core region of an atom and, therefore, has localized character like the deep-core electron in XAS. These localized electrons are backscattered from the near neighbors in a similar way as in EXAFS. In the case of monoatomic solids, the backscattering mechanism is the same for EXAFS and EXBIFS. For this reason, the EXBIFS can be quantitatively analyzed in analogy with EXAFS spectra. On the other hand, as no core-level excitation is involved in BIS, the phase shifts of the absorbing atoms in EXAFS can be studied.

To summarize, we have studied the matrix element effect in BIS for the extended energy region 50–380 eV above E_F. The numerical results for Cu and Pd are presented for two photon energies, 1487 and 5415 eV. We have found that the transition rate depends on atomic number, transition energy, and angular momentum quantum number of the final-state wave function. Consequently, an isochromat photon energy can be chosen for the purpose of studying a prepared mixture of the l components of the final state. We have demonstrated that the decelerated final electron originates in the core region of an atom and that the actual calculations only needs the atomic potential as an input and a choice of the transition energy. We have shown that EXBIFS arises in a similar way as in EXAFS, and the main information to be gained from studying fine structure is actually structural.

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