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Extended x-ray bremsstrahlung isochromat of Pd

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The x-ray bremsstrahlung isochromat of Pd has been measured up to 130 eV above the Fermi level for a photon energy of 5415 eV with a resolution of 1.8 eV. The fine structure of the Pd isochromat is interpreted as due to the density of *p*-type states according to the momentum-specific energy dependence of the transition probability. Fourier analysis was performed and an interatomic distance of 2.76 Å was obtained for Pd. The authors propose a simple formula for calculations of x-ray bremsstrahlung isochromats by using a factorization of an x-ray bremsstrahlung isochromat into atomiclike and solid-state contributions.

I. INTRODUCTION

Bremsstrahlung isochromat spectroscopy (BIS) is a method for investigating unoccupied electronic states in solids. In principle, any photon energy can be chosen for BIS measurements, but in practice only those photon energies are used for which a monoenergetic detector can easily be constructed. Until the present BIS instruments were constructed for the x-ray region (e.g., for a photon energy of 5415 eV equal to the Cr $K\alpha_1$ photon energy), the soft-x-ray region (e.g., for a photon energy of 1487 eV equal to the Al $K\alpha_{1,2}$ photon energy), and the ultraviolet region (e.g., for an energy of about 10 eV for the photon transmission edge of the CaF_2 window). (The ultraviolet bremsstrahlung emission is called inverse photoemission.)

The x-ray bremsstrahlung transitions probe all unoccupied electronic states of solids, giving us a picture of the electronic state distribution more or less similar to the total density of states (DOS) depending on whether the transition probability differs more or less between final states with different orbital angular momentum l numbers. Unfortunately, calculations of transition probabilities in an x-ray energy region have not been made even for an atomic state.

There have been several experimental works published treating the problem of whether or not the BIS spectra show the total DOS. For example, the BIS spectrum of Ni measured by Chu and Best[1] at a photon energy of 5415 eV was similar to the Ni K-edge x-ray-absorption spectrum and quite different from the BIS spectrum at 1214 eV, which was interpreted as the transition probability effect. On the other hand, the BIS spectra of the $3d$ and $4d$ transition metals measured by Speier *et al.*[2,3] at 1487 eV were similar (at least up to 10 eV above the Fermi level E_F) to the total DOS calculated by the same authors.

If the x-ray BIS spectrum favored the final states of p-type symmetry instead of the total DOS, then it could be possible to observe the extended x-ray bremsstrahlung isochromat fine structure (EXBIFS), similar to the extended x-ray-absorption fine structure (EXAFS). The first works on EXBIFS were done for Ge at a photon energy of 5415 eV by Sobczak *et al.*[4] and for Cu at 1487 eV by Speier *et al.*[5,6] It was found that the EXBIFS of Ge and Cu was similar to the K-edge EXAFS of Ge and Cu, respectively. However, a discussion of the EXBIFS of Ge and Cu still remains difficult for lack of theoretical data on the partial densities of states for Ge and Cu through an extended energy range.

In this work we have chosen Pd for EXBIFS studies, because for this metal there is presently available full information on the theoretical electronic band structure, including partial densities of states up to 140 eV above E_F, owing to the unique work of Müller and Wilkins.[7]

II. EXPERIMENTAL DETAILS

We have measured the BIS spectrum of Pd at a photon energy of 5415 eV by using an apparatus consisting of a dismountable x-ray tube, a well-stabilized high-voltage supply, and a vacuum x-ray spectrometer. In comparison to our previous work[4] the instrument has presently much higher resolution owing to the new Si(220) monochromator of Johann type and a new high-voltage control system.

The Si(220) dislocation-free crystal was bent cylindrically to a 1-m radius of curvature. The calibration of the spectrometer was performed by use of the Cr $K\alpha_1$ emission line (5414.72 eV) from a Cr platelet excited by 7.4-keV electrons. The measured full width at half maximum (FWHM) of the Cr $K\alpha_1$ line was 3.3 eV, while the natural width of this line is 2.07 eV.[8] The advantage of using a proportional counter as a detector was a very low background equal to 16 counts/min. The vacuum in the x-ray tube was in the range 10^{-4} Pa. The electron-emission current from the directly heated thoriated tungsten cathode was 11 mA.

The sample has been cut from a 0.2-mm foil of 99.99%-pure Pd and mounted on a water-cooled holder in a special way, to protect the middle part of the sample—being under electron bombardment—from direct contact with a cooled holder. This resulted in a constant temperature of about 1300 K within the investigated area. Due to the high temperature of the Pd sample one could avoid the carbon and oxygen contamination[9] during a long-time measurement. The influence of surface contamination on the BIS spectrum seems to be negligible, even in the soft-x-ray BIS spectrum of Pd measured in a vacuum of 10^{-5} Pa and a temperature of 1400 K,[10] which can be seen by comparing Pd isochromats from Refs. 10 and 3.

III. RESULTS

The near-threshold BIS spectrum of Pd up to 20 eV above E_F has been measured in 0.2-eV steps and summarized after six scans. The result shown in Fig. 1 agrees well with the earlier data published by Liden.[11] From a broadening of the BIS threshold we have estimated the width, FWHM = 1.8 eV, of the total spectrometer function including the monochromator window, the energy spread of electrons emitted from the cathode, and the width induced by the lifetime of the initial electron state in Pd. The width of the final electron state close to the Fermi level was assumed to be negligibly narrow.

The broadening of the BIS threshold of Pd in our experiment is much smaller than the broadening of Pd L_1 and Pd K absorption edges, because the natural width of the Pd L_1 and Pd K hole levels is equal to 6 and 6.8 eV, respectively.[7] This advantage of the BIS spectrum is shown in Fig. 1, where the BIS spectrum of Pd is compared with the Pd L_1 x-ray-absorption near-edge structure (XANES) obtained by Davoli *et al.*[12] using synchrotron radiation.

The BIS spectrum of Pd in an extended energy range has been measured up to 130 eV above E_F in 0.5-eV steps and summarized after 13 scans. The result presented in Fig. 2 shows that the BIS spectrum of Pd has really an extended fine structure.

In order to compare the BIS fine structure with the theoretical DOS of Pd,[7] we have found a smooth curve $A(E)$,

$$A(E)=C_1[(E-E_0)^{1/2}+0.113E]\ , \qquad (1)$$

where C_1 is a constant, that displays the general shape of the BIS spectrum of Pd. Here, E denotes the energy (in eV) of the final state with respect to Fermi energy E_F, and $E_0=-7$ eV is the energy of the bottom of the valence band of Pd. In a very rough simplification the first term in Eq. (1) can be explained as the BIS intensity approximated by the free-electron DOS, whereas the second term would be the BIS intensity produced by inelastically scattered electrons.

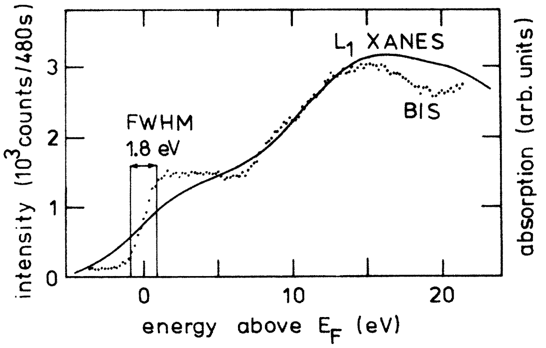

FIG. 1. Comparison of the x-ray BIS spectrum of Pd (dots) and the L_1 XANES spectrum of Pd (solid line) obtained by Davoli *et al.* (Ref. 12) using synchrotron radiation.

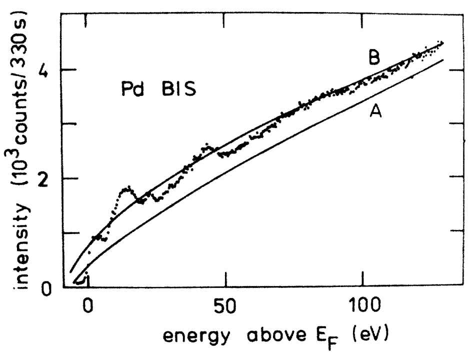

FIG. 2. X-ray bremsstrahlung isochromat of Pd at a photon energy of 5415 eV measured in an extended energy range (dots) and arbitrary curves A and B (solid lines) fitted to the general shape of the Pd isochromat.

In Fig. 3 a curve is presented that shows the difference between the BIS spectrum and the function $A(E)$, together with the total and p-type partial densities of states of Pd. We have observed that the fine structure of the BIS spectrum of Pd is strikingly similar to the p partial DOS and also similar to the EXAFS above the Pd L_1 and Pd K edges,[13] but very different from the total DOS. Therefore we have tried to calculate the Fourier transform of the Pd EXBIFS by using a method similar to the EXAFS analysis. First, we have found another smooth curve, $B(E)$, running in between the maxima and minima of the BIS intensity in the following form:

$$B(E)=C_2[(E-E_0)^{1/2}+0.003E]\ , \qquad (2)$$

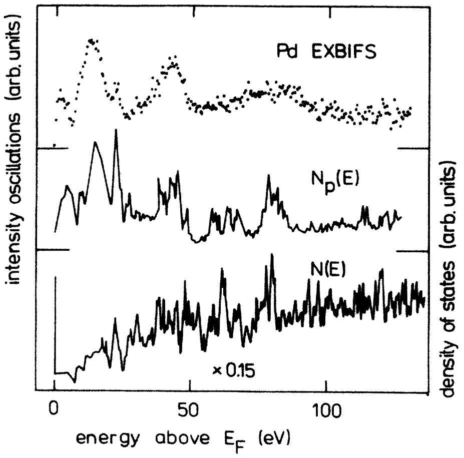

FIG. 3. Fine structure of the BIS spectrum of Pd (dots) compared with total and p partial densities of states in Pd from Ref. 7 (solid line).

where C_2 is a constant. Then we calculated the difference between the BIS spectrum and $B(E)$, and transformed the curve from the energy scale into the wave-number-k scale by using the relation $k(\text{Å}^{-1})=[0.263(E-E_0)]^{1/2}$. The resulting EXBIFS curve is shown in Fig. 4. After multiplying the EXBIFS by k^3, we calculated the Fourier transform in the range between $k_{\min}=2.00$ Å^{-1} and $k_{\max}=5.95$ Å^{-1}.

The magnitude of the Fourier transform as a function of R is shown in Fig. 5. The maximum at $R=0$ Å has no physical meaning. The second maximum at $R=1.4$ Å can be explained by (a) Ramsawer-Townsend modulation of the backscattering amplitude,[14] and (b) the Pd-O interatomic distance of the surface-contamination oxide. Other authors, who have obtained a similar peak in the L_1 EXAFS analysis of Pd,[13,15,16] discussed only the Ramsawer-Townsend effect. The main peak at $R=2.50$ Å is due to the nearest-neighbors atoms in Pd. After a phase-shift correction of 0.26 Å taken from EXAFS results, we obtained the value of 2.76 Å for the interatomic distance in Pd, which is in good agreement with the crystallographic data of 2.74 Å. A broad maximum at $R=4.5$ Å is due to the second- and third-neighbor atoms. A broadening of peaks is caused by the high temperature of the sample during measurements and by a relatively narrow energy range of the measured EXBIFS.

Our Fourier analysis of the EXBIFS spectrum of Pd has shown unambiguously that the BIS spectrum of Pd at a photon energy of 5415 eV corresponds to the Pd L_1 and Pd K x-ray-absorption spectra. The reason for this correspondence is discussed below.

IV. DISCUSSION

X-ray bremsstrahlung experiments and theories have shown[17] that the intensity of the x-ray bremsstrahlung spectrum is proportional to Z^2 for very thin targets. Therefore we conclude that acceleration of the incident electron must be mostly affected by the part of the potential close to the nucleus.

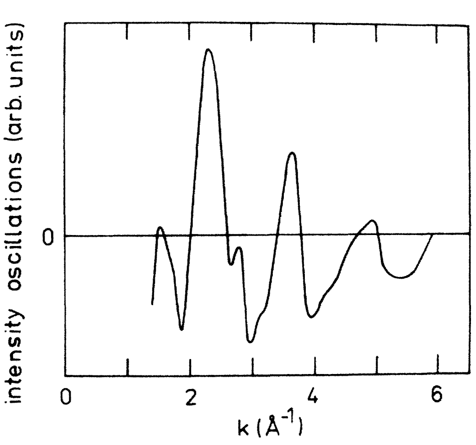

FIG. 4. EXBIFS of Pd (being a difference between the BIS spectrum and curve B in Fig. 2) shown as a function of wave number k.

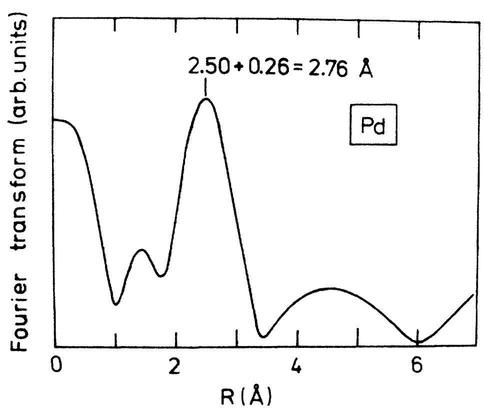

FIG. 5. Magnitude of the Fourier transform of the Pd EXBIFS with the main peak showing the nearest-neighbor interatomic distance of 2.76 Å in Pd.

Electrons with the initial energy E_i incoming to a polycrystalline solid sample produce the x-ray bremsstrahlung radiation—its intensity in the dipole approximation and the direct-transition approximation taken for the constant photon energy ω is proportional to the spectral distribution of the oscillator strength $F(E_i,\omega)$ given by the formula (in a.u.)

$$F(E_i,\omega)=\frac{\omega}{3}\sum_{\mathbf{k},j,h}|\langle\psi_{f,\mathbf{k},h}|\mathbf{r}|\psi_{i,\mathbf{k},j}\rangle|^2 \times\delta(E_{i,\mathbf{k},j}-E_{f,\mathbf{k},h}-\omega) \times\delta(E_{i,\mathbf{k},j}-E_i)\ , \tag{3}$$

where $\mathbf{k}$ is the reduced wave vector, $\psi_{i,\mathbf{k},j}$ and $\psi_{f,\mathbf{k},h}$ are wave functions of the initial and final electron states, respectively, $E_{i,\mathbf{k},j}$ and $E_{f,\mathbf{k},h}$ are energies of the initial and final states, and j and h denote the number of a band.

Computation of an x-ray BIS spectrum from the band-structure calculations of $E_{\mathbf{k},j},\psi_{\mathbf{k},j}$ according to Eq. (3) is practically impossible owing to a large number of energy levels for each reduced vector $\mathbf{k}$ in the high-energy region. In this work we propose a simple formula for calculation of a BIS spectrum.

We start from an assumption that the spatial domain of x-ray bremsstrahlung transitions not far from the short-wavelength limit is the space between the nucleus and the 1s orbital, which means that the x-ray bremsstrahlung transition is localized in a similar way as the x-ray-absorption transition involving a 1s electron. So we can adopt a formalism of a factorization of a spectrum into atomiclike and solid-state contributions developed by Müller and Wilkins[7] for x-ray-absorption spectra.

The x-ray bremsstrahlung transition probes all l components of the final state E simultaneously; therefore we express the oscillator strength $F(E_i,\omega)$ as a sum of l-projected oscillator strengths $F_l(E_i,\omega)$:

$$F(E_i,\omega)=\sum_l F_l(E_i,\omega)\ . \tag{4}$$

Each $F_l(E_i,\omega)$ contribution can be decomposed into atomiclike and solid-state terms:

$$F_l(E_i,\omega)=F_l^{\text{at}}(E_i,\omega)\frac{N_l(E)}{N_l^{\text{at}}(E)} . \tag{5}$$

Here the dipole transition strength $F_l^{\text{at}}(E_i,\omega)$ connecting the initial state E_i to the l orbital in an isolated atom is proportional to the following term:

$$F_l^{\text{at}}(E_i,\omega)\propto[l\langle\phi_{E_i,l-1}^{\text{at}}\,|\,\mathbf{r}\,|\,\phi_{E,l}^{\text{at}}\rangle^2 +(l+1)\langle\phi_{E_i,l+1}^{\text{at}}\,|\,\mathbf{r}\,|\,\phi_{E,l}^{\text{at}}\rangle^2] , \tag{6}$$

where $\phi_{E,l}^{\text{at}}$ is the radial part of the lth partial wave function for an electron with a positive energy E in an isolated atom.

The l-projected density of band states, $N_l(E)$, in the final state E is defined as

$$N_l(E)=2\sum_{\mathbf{k},h}\sum_m|\langle Y_{lm}\,|\,\psi_{f,\mathbf{k},h}\rangle|^2\delta(E-E_{f,\mathbf{k},h}) . \tag{7}$$

The l-projected density of states $N_l^{\text{at}}(E)$ for an atom is defined as

$$N_l^{\text{at}}(E)=\frac{1}{\Omega}(2l+1)N^{\text{FE}}(E)\langle(\phi_{E,l}^{\text{at}})^2\rangle , \tag{8}$$

where Ω is the volume of integration and $N^{\text{FE}}(E)$ is the free-electron density of states at energy E. The ratio

$$\chi_l(E)=\frac{N_l(E)}{N_l^{\text{at}}(E)} \tag{9}$$

is a solid-state contribution that is well known as the extended x-ray-absorption fine structure (EXAFS).

It would be interesting to discuss the dependence of the oscillator strength $F_l^{\text{at}}(E_i,\omega)$ on the initial energy E_i and photon energy ω. As yet, no calculations of $F_l^{\text{at}}(E_i,\omega)$ have been made for neutral atoms in the x-ray energy region. If one takes a simplified problem of hydrogenlike ions, then the radial matrix elements for continuum-bound transitions can be evaluated analytically. Within the limits of this simplification, we could easily calculate ionic oscillator strengths $F_l^{\text{IO}}(E_i,\omega)$ for Pd ions with $Z_{\text{eff}}=23$ and for the energy E_i varying from 300 eV up to 10 000 eV by using the effective-charge approximation and the scaling property proposed by Hahn and Rule.[18] We have found that all values of $F_l^{\text{IO}}(E_i,\omega)$ decrease with increasing energy E_i and the rate of decrease becomes larger with l number. Results of calculations for the two energies $E_i=1480$ and 5415 eV presented in Table I show the l-specific energy dependence of matrix elements for the x-ray bremsstrahlung transitions. It qualitatively explains the fact that in an energy range up to 10 eV above E_F the shape of the BIS spectrum of Pd at 1487 eV reflects the total DOS,[2,3] consisting for the most part of s, p, and d states, because at this photon energy the transition probabilities for s, p, and d states are comparable. However, in an extended energy range the BIS spectrum of Pd (Ref. 3) does not reflect the total DOS. For example, the experiment does not show a maximum of the density of f states at an energy of about 50 eV above E_F, which is predicted by theory,[7] due to the low probability of electron transitions into f states (see Table I).

The results shown in Table I also qualitatively explain the fact that our BIS spectrum of Pd measured at a photon energy of 5415 eV reflects both s and p partial densities of states rather than the d partial density of states, because the transition probabilities for s and p states dominate over those for d, f, and g states. We cannot distinguish between s and p contributions to our BIS spectrum of Pd, because both s and p partial densities of states have main maxima positioned at nearly the same energies.[7]

V. CONCLUSIONS

We have shown that the initial electron state in Pd at the energy of 5.4 keV has an energy width well below 1.8 eV. The possibility of high-resolution studies of occupied electron states makes x-ray BIS spectroscopy interesting, compared to x-ray-absorption spectroscopy.

The BIS spectrum of Pd at a photon energy of 5415 eV measured within an extended energy range contains the fine structure that is similar to the L_1 or K EXAFS structures of Pd, while the BIS spectrum of Pd at a photon energy of 1487 eV, from Ref. 3, shows characteristic features of both L_1 and L_3 x-ray-absorption spectra of Pd. This striking difference is due to a specific energy dependence of the transition probability for different orbital angular momenta of the final electron state.

A strong energy dependence of matrix elements in BIS spectra constitutes a difficulty in interpretation of spectra, but, on the other hand, it gives us a chance to choose a suitable photon energy for BIS studies. It seems from this work that the photon energy of 5415 eV is well suited for the structural analysis of the EXBIFS spectrum of Pd.

For the interpretation of the EXBIFS spectra we propose a general formula by using a factorization of a BIS

TABLE I. The l-projected oscillator strengths F_l^{IO} (normalized to the $l=2$ contribution) calculated for Pd ions and the initial energy E_i.

E_i			F_l^{IO}		
(eV)	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
1480	1.05	1.53	1.00	0.30	0.04
5415	2.36	2.61	1.00	0.19	0.001

spectrum into atomiclike and solid-state contributions. The precise calculations of atomic transition probabilities necessary for interpretation of BIS spectra seem to be possible nowadays, so one should hope that they will be made in the near future.

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