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Photon cross sections near the x-ray-absorption edges of Ti, Ni, Pt, and Au

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Absolute photon absorption spectra at the *K* edges of Ti and Ni and at the L_3 edges of Pt and Au, recorded using synchrotron radiation, are reported. The average photon cross section at L_3 edges of Pt and Au are found to be in general agreement with the theoretical data of Scofield. A possible explanation of why such agreement is not found for Ti and Ni at *K* edges is presented.

INTRODUCTION

With the advent of synchrotron radiation, the oscillatory behavior of the photon absorption coefficient near edges and its interpretation in terms of local electronic and structural properties around the absorbing atom are today well established.[1,2] In fact the x-ray-absorption near-edge structure (XANES) extending up to 20 eV or so above the edge is mainly due to electronic transitions to unfilled states above the Fermi level, thus resembling the unoccupied density of electronic states projected on the absorbing atom.[3] The more extended structure from 20 eV up to nearly 1000 eV above the edge is due to interference effects on the photoelectron, by the local spatial ordering of the neighboring atoms [the so-called extended x-ray-absorption fine-structure spectroscopy (EXAFS) modulation[4]].

The fine structure is relevant also in photon absorption cross-section measurements. Kerr *et al.*[5] in a study of the cross section at *K* edges of 3*d* elements from Ti to Zn using an x-ray tube observed that on average the experimental *K*-edge cross sections are higher than the available theoretical data. Since their contribution suffers from the presence of the fine structure, attempts[6,7] have been made to check the theoretical data by extrapolating the absorption cross sections measured a few keV above the edge towards the edge itself and found an agreement, more or less, with the two available theoretical calculations of Storm and Isreal[8] and Scofield[9] at the respective edges. The aim of the present investigation is to check experimentally for the first time Scofield's[9] theoretical photon cross sections at *K* edges of Ti and Ni and at L_3 edges of Pt and Au using synchrotron radiation by averaging the data to remove the oscillatory fine structure of the absorption coefficient.

EXPERIMENT

Measurements have been performed at the Frascati synchrotron radiation facility PLUS.[10] The x-ray beam emerging from the Adone storage ring is sent to the experimental area 17 m away, through high-vacuum pipes. Here, after a 75-μm Be window, the radiation is monochromatized by a Si(111) asymmetric channel cut crystal. The beam then enters a collimator (2-mm-diam hole) and passes through two ionization chambers, the sample holder being in between them. To avoid any scattering and fluorescence radiation reaching the second detector, another collimator (5-mm-diam hole) is placed between the second detector and the sample holder. The ionization chambers were filled with Ar gas. The samples were high-quality thin foils of Ti, Ni, Pt, and Au (Goodfellow Metal Company UK). The spectra on the Ti and Ni *K* edges and on Pt and Au L_3 edges have been recorded with and without samples, employing procedures already in use. Subtracting the $\ln(I_0/I_s)$ obtained without the sample to the one with the sample the absolute spectra are obtained (I_0 and I_s being the currents of the ionization chambers before and after the sample, respectively).

RESULTS AND DISCUSSION

The raw absorption spectra are shown in Fig. 1. In order to compare the spectra with the theoretical data the energy scale has been normalized at the point of inflection with the edge energy reported by Storm and Isreal[8] (unique edge). Moreover, the spectra have also been normalized ranging from 400 to 800 eV above the edge using the theoretical total photon cross sections (at 5500 eV for Ti, at 9000 eV for Ni, and at 12 320 eV for Pt, and Au, respectively). Indeed, at these energies the theoretical total photon cross sections are supposed to be, more or less, in agreement with the experimental data and the contribution of the fine structure can be almost neglected.[6,7,11] It can be seen from Fig. 1 that at and above these energies of normalization, the oscillatory behavior is in general negligible and it is not substantial when compared to the experimental errors. Such a normalization procedure eliminates the errors particularly due to uncertainties in the weight and the nonuniformities of the foils, scattering, and fluorescent radiation effects and gives accurate values at the edges. We have to remark here that in the above normalization procedure and in the following comparisons we use the total photon cross sections obtained by adding the accurate theoretical scattering cross sections[12,13] to the theoretical photoelectric cross

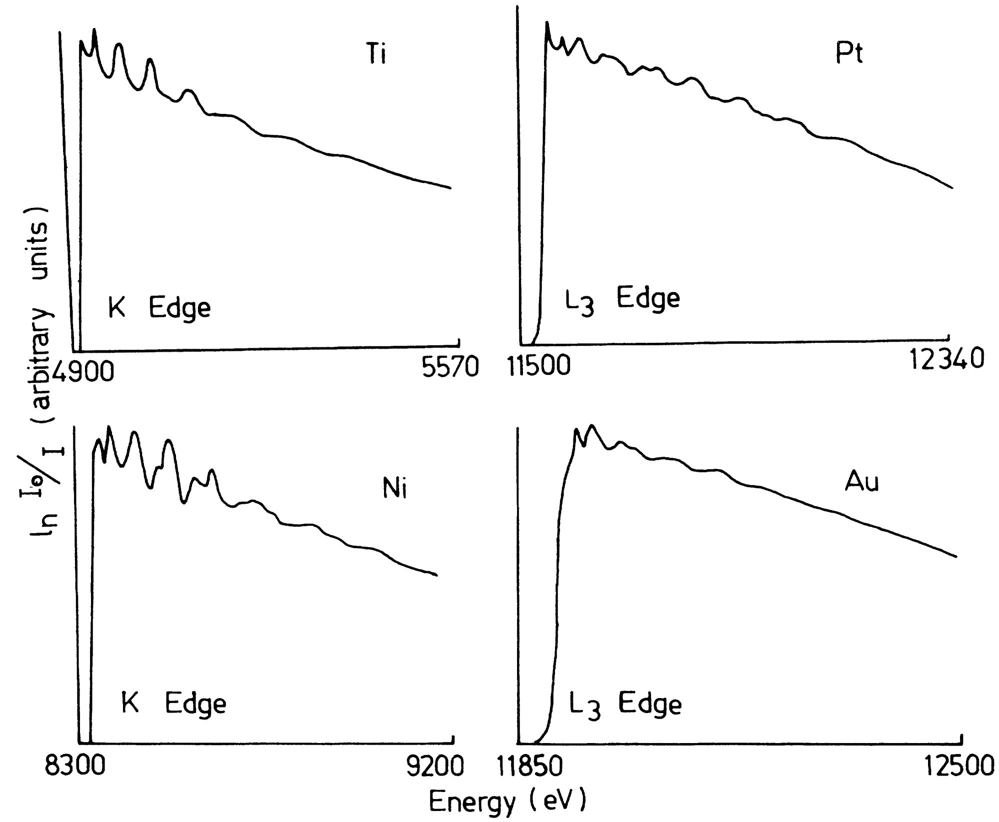

FIG. 1. Photon absorption spectra of Ti, Ni, Pt, and Au at absorption edges.

sections of Scofield.[9] In any case, since the scattering contribution is only of the order of 2% or less at these energies, we are essentially dealing with the photoelectric contribution. In Fig. 2 we report the so normalized experimental data. The total error in such data is of the order of 3% or less.

In Table I we compare our absolute cross sections including the oscillations with the values of Storm and Isreal[8] and Scofield.[9,12,13] Note how, excluding Ti data, a general agreement within a few percent is found with Scofield's[9] predictions at those exact energies. On the other hand, the rather large disagreement with Storm and

TABLE I. Photon cross sections (barns per atom). The cross section in the column labeled (1) is derived with oscillation. The cross section in the column labeled (2) is derived with a smooth line from the midpoints of the oscillations (Fig. 2) and the corresponding deviation from Scofield's theoretical data.

		Theory		Present work		
Element	Energy (eV)	Storm and Isreal[a]	Scofield[b]	(1) Error (~3%)	(2) Error (4%)	Deviation from Scofield's[b] theory (%)
Ti	5500	43 221	42 775	42 775[c]		
	4975.2 (upper *K* edge)		54 602	61 302	61 425	11.1
	4966.0 (unique *K* edge)	56 300		32 823		
Ni	9000	26 630	26 492	26 492[c]		
	8361 (upper *K* edge)		31 836	32 155	34 228	7.0
	8332 (unique *K* edge)	32 600		19 745		
Pt	12 320	53 612	53 248	53 248[c]		
	11 647 (upper L_3 edge)		61 817	59 945	60 644	1.9
	11 564 (unique L_3 edge)	63 800		44 098		
Au	12 320	56 020	55 979	55 979[c]		
	12 005 (upper L_3 edge)		59 967	59 123	58 749	2.1
	11 919 (unique L_3 edge)	61 200		42 287		

[a] Reference 8.

[b] Reference 9.

[c] Cross section used for normalization.

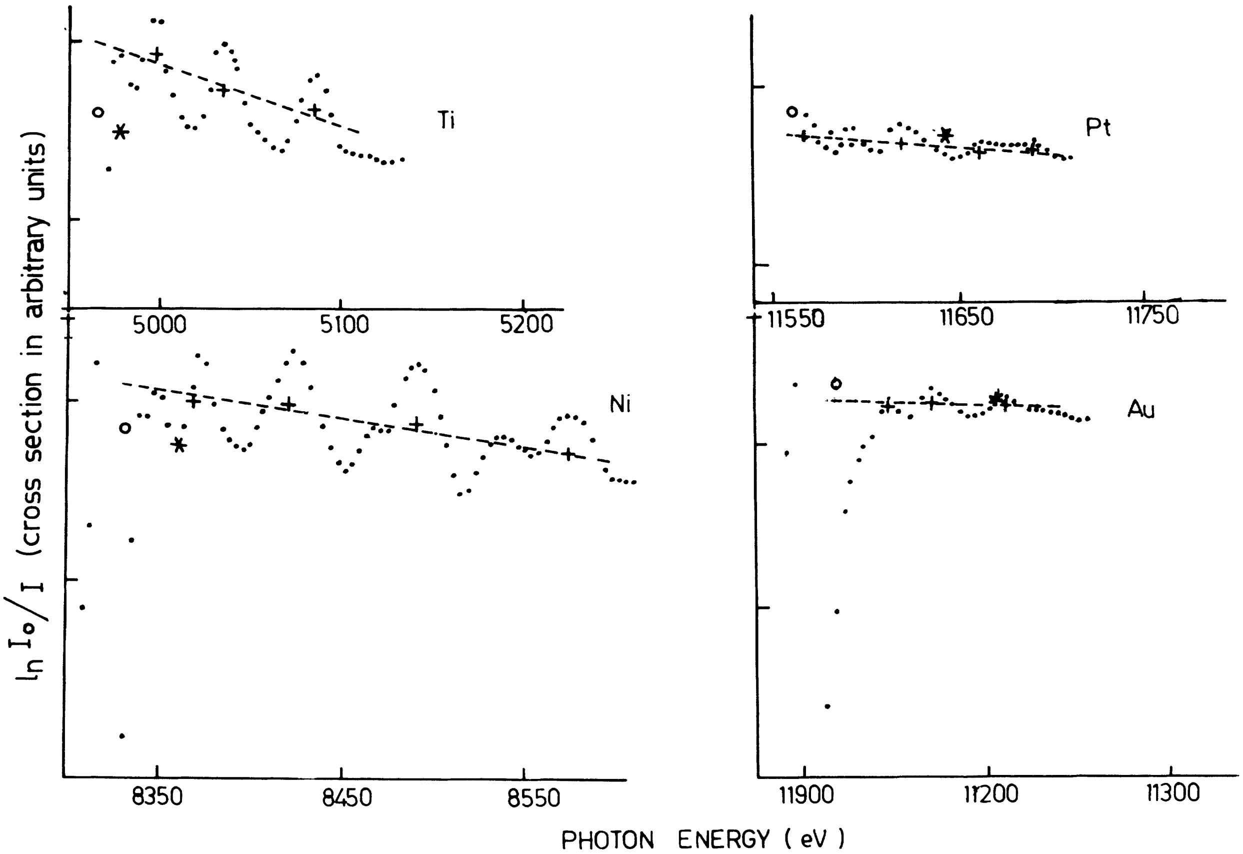

FIG. 2. Normalized photon absorption spectra of Ti, Ni, Pt, and Au very near to edges. ○, Storm and Isreal (theoretical data; Ref. 8); $*$, Scofield (theoretical data: Refs. 9, 12, and 13); — — —, average line drawn using the midpoints of the oscillations.

Isreal's data[8] at edges is certainly due to the presence of final-state effects at the energy values which are in the XANES fine-structure region. Look, for example, at the large first peak at the L_3 edge of Pt which is missing in Au. Such a peak has been attributed to a $1s$-$4d$ transition in Pt which is forbidden in Au for its $4d^{10}$ electron configuration.[14] As shown in both Figs. 1 and 2, and also, at Scofield's[9] upper-edge energies, the absorption cross section shows fine structure, and here we are in the EXAFS region, particularly for Pt and Au. In such a region it is possible to determine the pure atomic cross section free from the EXAFS effects by fitting the data with cubic splines.[1] Such procedures, routinely used in EXAFS data analysis, are based on the fact that the mean monotonic behavior of the absorption cross section is the pure atomic cross section. In our case we have drawn a line through the midpoints of the first few oscillations, obtaining the cross section at the Scofield's[9] upper-edge energies (Fig. 2) corrected for the EXAFS contribution. In Table I the values so obtained are also compared with Scofield's[9] theoretical data. It is evident that while a satisfactory agreement is found for Pt and Au, large discrepancies exist for Ti and Ni. This may be due to the fact that Scofield's[9] edge energies for Ti and Ni are more near the experimental unique edge and so they are in the XANES region. In this region the EXAFS data analysis procedures are not useful and more complex procedures should be used. In the case of Pt and Au, not only is the EXAFS effect seen to be less, but also Scofield's[9] upper-edge energies are in the EXAFS region.

In conclusion, we checked the accuracy of Scofield's[9] photon cross sections near edges for the first time using synchrotron radiation and have shown that there is general agreement between the theoretical and experimental cross sections, provided the XANES effect is less and the latter can be treated using EXAFS procedures to separate the atomic cross section from the extended fine structure as in the cases of Pt and Au. In addition, Scofield's[9] upper-edge energies are found to be more realistic in view of the finite level width observed.

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