PHYSICAL REVIEW B VOLUME 42, NUMBER 1 1 JULY 1990

3*p* and 3*d* core-level widths in metallic technetium: A study by internal-conversion electron spectroscopy

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(Received 27 July 1989)

3*p* and 3*d* core-level widths have been determined experimentally by the help of internal-conversion electron spectroscopy in metallic ^{99m}Tc. The Coster-Kronig broadening of an internal-conversion line has been identified in the case of the M_4 transition. The existence of chemical effects on the $3d_{3/2}$ core-hole lifetime is shown for NH_4TcO_4. From the measured energies of the conversion peaks and from the core-level binding energies obtained earlier by x-ray photoelectron spectroscopy, the value of the $E3$ transition energy has been determined to be 2173.8±0.4 eV. Application possibilities of the results in resolution calibration of electron spectrometers and for x-ray width determination are briefly discussed.

INTRODUCTION

The significance of the electron spectroscopic methods in experimental determination of core-level natural linewidths has been demonstrated in earlier works.[1-3] In most cases x-ray photoelectron spectroscopy (XPS) studies have been performed proving that solid-state and atomic and molecular contributions can be separated in the measured electron spectra by using adequate evaluation methods. For technetium an interesting possibility is given: Because the ^{99m}Tc nuclear isomeric state decays through the highly converted 2.17-keV $E3$ transition, the results of the XPS studies can be compared with the data obtained by internal-conversion electron spectroscopy (ICES), measuring the kinetic energies of the electrons emitted from radioactive atoms during the internal conversion process. Because of the sufficiently narrow conversion lines, ICES proved to be an efficient and sensitive technique for investigation of valence states of ^{99m}Tc and was considered as a "radioactive variant" of XPS (Refs. 4 and 5) with the advantage of having no broadening of the spectral lines due to the excitation. Apart from the change due to the different contribution of the inelastic electron scattering at differing peak energies and to the lack of the x-ray broadening, ICES and XPS core line shapes are expected to be the same. The purpose of this work is to examine the applicability of the ICES method for determining small inherent atomic level widths.

In the metals Nb–Rh the Coster-Kronig (CK) broadening of the $3d_{3/2}$ core levels were observed previously,[2,6] and the extent of this broadening is close to the maximum in the case of Tc, indicating the delocalized character of the $M_5N_{4,5}$ Auger final state. A strong chemical effect was also experienced on the Tc $3d_{3/2}$ CK broadening.[6] In this paper we present the results of the analysis of the $M_{4,5}$ ICES spectra (for brevity, we are referring so to the M conversion spectra of the 2.17-keV nuclear transition of ^{99m}Tc everywhere in the following) from metallic and NH_4TcO_4 samples and compare these results with the data obtained by XPS, applying the developed method for determination of the 3*p* level widths in metallic Tc. Using an energy calibration procedure based on XPS measurements, the energy of the $E3$ nuclear transition calculated from the measured conversion line energies and the core-level binding energies, is also presented.

EXPERIMENT

^{99m}Tc sources were prepared from a supplied ^{99m}Tc-sodium pertechnetate solution in saline. The solution was treated by an extraction and reextraction procedure to remove sodium chloride content.

Tc metal sources were prepared by electrolysis of pertechnetate in 4N sulphuric acid using a 50-μm thick platinum cathode of 0.5 cm^2 area and a platinum spiral anode. The applied voltage was between 2.7–2.9 V. The foil with the deposit was leached for one minute in boiling water and placed into vacuum.

For the NH_4TcO_4 sources, technetium was firstly electrodeposited in the form of dioxide from 3N potassium hydroxide solution. The applied voltage was 3.0 V. The dioxide deposit was oxidized by one drop of diluted nitric acid (1:10) and dried under an infrared lamp, then exposed to ammonia vapor for 5–10 minutes. The activity of the sources varied between 600–1200 MBq and the total amount of technetium was about 0.1 μg.

For identification of the chemical state of Tc, and for energy calibration the XPS method was applied. ICES and XPS measurements were performed in an electrostatic electron spectrometer[7] equipped with an Al anode x-ray tube (9 kV, 20 mA) using a 2-μm thick Al window. Electron spectra were measured in fix analyzer transmis-

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sion (FAT) working mode at 60-eV passing energy with full slit opening, corresponding to an instrumental resolution of about 1 eV. The time necessary to introduce the ready sample into the vacuum chamber of the spectrometer was typically 2–3 min and the oil-free vacuum during the measurements was better than 10^{-5} Pa.

Energy calibration of the spectra was made with the help of vacuum-evaporated gold and scraped Cu sample introduced into the spectrometer under dry nitrogen envelope. XPS spectra of the Au $4f$, Cu $2p$, and C$1s$ lines of the calibrants were recorded, while in the case of technetium samples Tc $3d$ and C $1s$ photoelectron peaks were measured. Spectrometer voltages were observed by using a high-precision Systems Voltmeter Solartron 7061 and by a precise high-voltage divider developed at Nuclear Physics Institute, Řež. For energy calibration the Au $4f_{7/2}$ and Cu $2p_{3/2}$ binding energies, obtained by Anthony and Seah,[8] were used. In the case of each calibrant and technetium sample a value of 285.0±0.05 eV was determined for the binding energy of the C $1s$ photoelectron peak originating from the surface contamination layer, indicating no need for charging correction.

RESULTS AND DISCUSSION

Figure 1(a) shows an $M_{4,5}$ conversion spectrum from a metallic ^{99m}Tc sample. There is a noticeable broadening of the M_4 line in the spectrum and both lines are asymmetric in their low kinetic-energy part. These features can be attributed to physical processes taking place in metals during core ionization. In metals Nb–Rh the $M_4M_5N_{4,5}$ Coster-Kronig process is allowed[2] and this process shortens the lifetime of the $3d_{3/2}$ hole considerably and causes a broadening of the inherent level width.

The asymmetry of the lines can be interpreted as a consequence of the interaction of the potential of the core hole in a metal with the conduction electrons.[9] To our knowledge, this is the first observation of the presence of the contribution of the above-mentioned solid-state effects in an internal-conversion spectrum.

Chemical states of the technetium samples were identified by XPS measurements of the Tc $3d_{5/2}$ binding energies. In the case of metallic samples, the $3d_{5/2f}$ binding energies were found to agree with the value of 253.9 eV obtained previously by different authors[6,10,11] within ±0.1 eV.

In determination of the extent of the lifetime broadening of the Tc $3d_{3/2}$ level in technetium metal by ICES, it is important to know the M_5-to-M_4 relative internal conversion coefficient (ICC), which gives the relative probability of the conversion processes, and the expected chemical effect on this relative probability. Hartmann *et al.*[12,13] calculated the effect of the chemical environment on the respective ICC's and found it to be negligible for the $M_{2,3}$ and $M_{4,5}$ transitions. On the basis of this result no observable effect is expected for the M_3-to-M_2 and M_5-to-M_4 relative ICC's.

From theoretical calculations[14,15] a relative ICC value of 1.51 can be computed for the M_5-to-M_4 rate, while for the M_3-to-M_2 conversion rate the respective relative ICC values are 1.76 (Ref. 15) and 1.77 (Ref. 14). The determination of the lifetime broadening of the Tc M_4 conversion line relies on the assumption that (except of this broadening) the line shapes of the two spin-orbit components (M_4 and M_5) are similar. Since the lifetime broadening corresponds to a folding by a Lorentzian, a simple self-deconvolution procedure[2] can be used for obtaining the value of the broadening. In order to reach a higher level of accuracy, a modified and automated version[16] of this procedure was used, and as a result a value of 0.35±0.05 eV has been determined for the Coster-Kronig broadening (Γ_{CK}) of the ^{99m}Tc M_4 internal conversion line (Table I), with the parameters of the spin-orbit energy separation $\Delta E_{\mathrm{so}} = 3.68$ eV and of the conversion intensity ratio $I_{M_5}/I_{M_4} = 1.50$. This Γ_{CK} value is in good agreement with the result

$$\Gamma_{\mathrm{CK}}(\mathrm{XPS}) = 0.39 \pm 0.05 \text{ eV}$$

obtained earlier[16] for the CK broadening of the $3d_{3/2}$ photoelectron line in Tc metal.

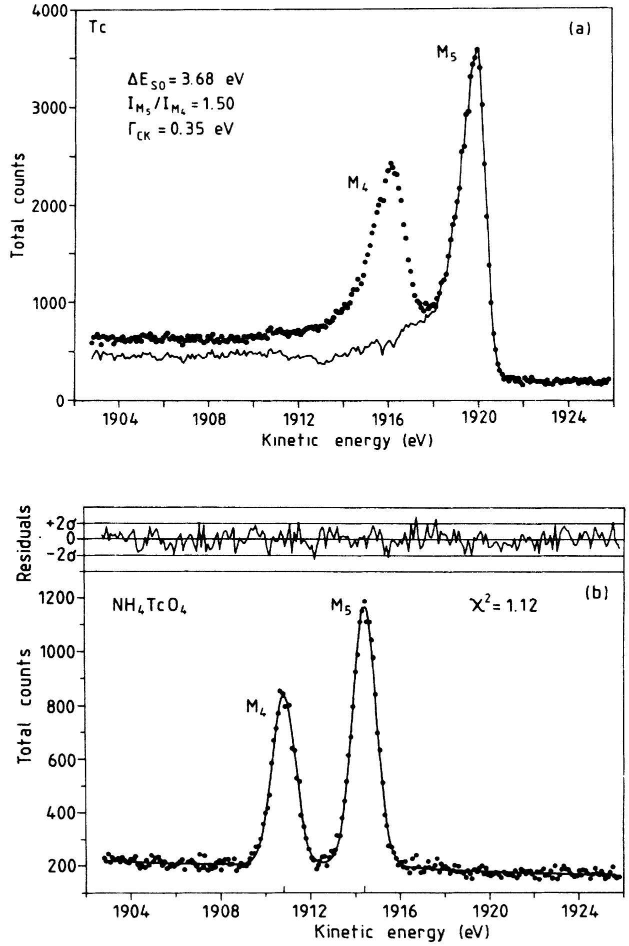

FIG. 1. (a) The $M_{4,5}$ conversion spectrum (●) from a metallic ^{99m}Tc sample; the result of the deconvolution of the broader M_4 line is shown by a continuous line. (b) The $M_{4,5}$ conversion spectrum from a NH_4TcO_4 sample (●), fitted (continuous line) by Voigt profiles and a linear background.

The core-level width (Γ_A) of the $3d_{5/2}$ level in metallic Tc can be well approximated by the following simple formula:[2]

$$\Gamma_A = \frac{5\Gamma_{\mathrm{CK}}}{2I_A - 3}, \tag{1}$$

where I_A is the $M_5N_{4,5}N_{4,5}$-to-$M_4N_{4,5}N_{4,5}$ Auger intensity ratio in Tc metal. Using the value of 8.4±3.4 for I_A measured by x-ray Auger excitation,[16] (1) gives 0.13±0.10 eV for Γ_A compared to the value of 0.14±0.10 eV obtained using XPS.[16]

The similarity of the Γ_{CK} values from ICES and XPS measurements proves that the broadening of the M_4 conversion line is due to the $M_4M_5N_{4,5}$ Coster-Kronig process in Tc metal and it also indicates that the ICES method is applicable for studies of Tc level widths.

Figure 1(b) shows the $M_{4,5}$ conversion spectrum of a NH_4TcO_4 sample. Both lines seem to be fairly symmetric with no significant broadening of the M_4 line. Applying the described modified self-deconvolution procedure, an upper limit of 0.05 eV has been found for Γ_{CK} (Table I), demonstrating that chemical effects on core-hole lifetime are also strongly reflected in the conversion spectra.

In the case of metallic Tc samples, there is no indication of a CK contribution to the M_2 conversion spectrum analyzed similarly (Table I, with $\Delta E_{so} = 19.8$ eV and $I_{M_3}/I_{M_2} = 1.70$). For determining the 3*p* core-level widths in Tc metal, it was assumed that the shape of the $M_{2,3}$ conversion lines is similar to that of the M_5 line except for a lifetime (Lorentzian) broadening. Folding the measured asymmetric M_5 conversion line with Lorentzians of different widths and comparing the line shape obtained this way to the measured $M_{2,3}$ lines (Fig. 2), the optimum fits give the differences between the $3d_{5/2}$ and $3p_{1/2}$ or $3p_{3/2}$ level widths and make possible the determination of the 3*p* core-level widths (Table I).

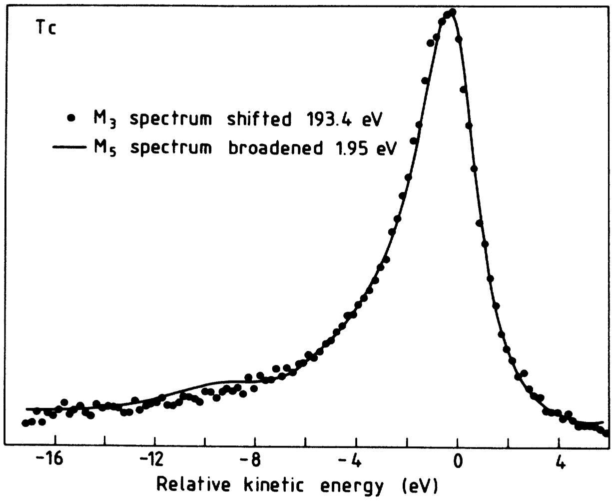

FIG. 2. The M_3 conversion spectrum (●) from a metallic ^{99m}Tc sample; the continuous line represents the shape obtained by folding the respective M_5 spectrum [Fig. 1(a)] with a Lorentzian having an FWHM of 1.95 eV.

In Fig. 3 our results are shown together with the experimental data obtained earlier for several neighboring elements[1,2,17] and with the one-electron-model Hermann-Skillman-type calculations of McGuire[18] and Ohno's calculations[19] based on the free-atomic frozen Hartree-Fock V^{N-2} potential approximation, which take into account the effects of the localized final-state double holes created following Auger electron ejection. Regarding the absolute value of the 3*p* level widths, our results do not con-

TABLE I. Core-level widths, Coster-Kronig broadenings, and transition energies determined in this work compared with data published in other studies. Γ_A is the level width; Γ_{CK} is the Coster-Kronig broadening; E_C is the kinetic energy of electrons converted from the core level indicated plus spectrometer work function; E_B is the core-level binding energy; $E_{\mathrm{tr}} = E_C + E_B$ is the energy of the *E*3 nuclear transition.

		Γ_A (eV)	Γ_{CK} (eV)	E_C (eV)	E_B (eV)	E_{tr} (eV)
Tc metal	$3p_{1/2}$	2.08(15)	<0.05	1726.5(2)	447.6(2)[b]	2174.1(4)
				1725.1(2)[c]	447.4(2)[c]	2172.5(4)[c]
	$3p_{3/2}$	2.08(15)		1746.3(2)	427.9(2)[b]	2174.2(4)
				1744.9(2)[c]	427.6(2)[c]	2172.5(4)[c]
	$3d_{3/2}$	0.48(10)	0.35(5)	1916.1(2)	257.5(2)[b]	2173.6(4)
			0.39(5)[a]	1915.3(2)[c]	257.5(2)[c]	2172.8(4)[c]
	$3d_{5/2}$	0.13(10)		1919.9(2)	253.9(2)[b]	2173.8(4)
		0.14(10)[a]		1918.9(2)[c]	253.9(2)[c]	2172.8(4)[c]
					253.9(2)[d]	
NH_4TcO_4	$3d_{3/2}$		<0.05	1910.8(2)		
	$3d_{5/2}$			1914.4(2)	258.9(2)[c]	2173.3(4)
					258.8(2)[d]	

[a] Reference 16.
[b] Reference 6.
[c] Reference 10.
[d] Reference 11.

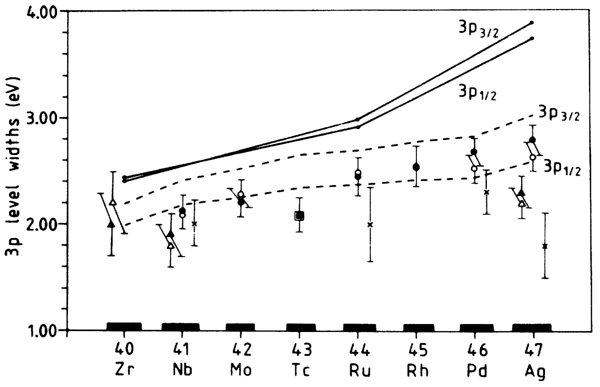

FIG. 3. 3*p* line widths for the elements Zr-Ag. Open symbols: $3p_{1/2}$, solid symbols: $3p_{3/2}$; (——) theory, McGuire (Ref. 18); (— — —) theory, Ohno (Ref. 19) (V^{N-2}); (○) Mårtensson and Nyholm (Ref. 2); (△) Yin *et al.* (Ref. 17); (×) Fuggle and Alvarado (Ref. 1) ($\Gamma_{1/2}=\Gamma_{3/2}$); (□) present work.

tradict the earlier experimental observations of neighboring elements and the general tendency of the dependence of these widths on the atomic number. It is necessary to note, however, that our data have slightly but significantly lower values than can be expected for Tc from the measurements of Mårtensson and Nyholm.[2] The Tc 3*p* natural level widths determined by us slightly differ also from the results of the calculations available,[18,19] although the results of the calculations[19] with correlation effects are considerably closer to the experimental data. In the latter case, however, the differences between the $3p_{1/2}$ and $3p_{3/2}$ level widths are too large, compared with the experiments, while the approximation of McGuire[18] reproduces these differences quite well.

From the energy measurements of the conversion electrons, using the core binding energies published,[6] the energy of the $E3$ nuclear transition can be estimated. For the determination of the conversion peak energies, the shape of the electron lines and the inelastic background have to be approximated in order to get a reliable fit of the assumed distributions to the experimental data.

In the case of the metallic sample, except for Lorentzian broadenings, the same line shape was used for all conversion lines as for the M_5 line. The M_5 line was fitted by a line shape that is asymmetric due to the interaction of the core hole with conduction electrons and obtained by Doniach and Sunjic,[20] and folding this asymmetric function with a Gaussian representing the instrumental broadening. The fitting resulted in practically the same value of the singularity index for all lines ($\alpha=0.20\pm0.05$). For inelastic background correction, the method of Tougard[21] was applied and the optimization of the line and background fitting parameters was done in the same procedure. Instead of DS, symmetric Voigt line shapes were fitted to the lines from the pertechnetate samples using linear background correction.

The results of the conversion energy measurements are summarized in Table I, where the respective binding energies and the computed $E3$ transition energies are also shown, in comparison with the those obtained by Gerasimov *et al.*[10] As an average, a value of 2173.8±0.4 eV has been determined from our data for the $E3$ nuclear transition energy in ^{99m}Tc. This value is more than 1 eV larger than the value of 2172.6±0.4 eV found earlier.[10] The weighted mean from all experimental data is 2173.3±0.3 eV. ^{99m}Tc M_5 conversion lines can be used for resolution calibration of electron spectrometers. They have the advantage of a low (~0.1 eV) contribution from the inherent core-level width and practically no contribution from the "excitation," e.g., from the inherent width of the nuclear isomeric state. A symmetric line shape is ensured by applying a pertechnetate sample for calibration. The calibration can be performed[22] either by deconvoluting the known-width Lorentzian from the measured M_5 spectrum leaving the contribution characteristic of the spectrometer, or by convolution of the same Lorentzian with Gaussians of different widths and by comparing the results of convolutions to the measured M_5 conversion spectrum. In the latter case the instrumental function is approximated by a Gaussian.

Natural widths of several-keV x-ray transitions can be determined by comparing the ICES and the XPS spectra from the same core level excited by the corresponding x rays. ^{99m}Tc conversion lines are narrow enough for this purpose.

SUMMARY

In summary, our studies prove the existence of strong solid-state effects on the metallic ^{99m}Tc M_4 internal conversion line. The value of the M_4 broadening (relative to the M_5 line) determined from the conversion spectra agrees with the value of the Coster-Kronig broadening of the $3d_{5/2}$ core level, found by XPS in technetium metal.

To our knowledge, this is the first observation of the Coster-Kronig broadening of a conversion electron line. The asymmetric conversion line shapes in metallic technetium can be successfully reproduced by the DS line shape obtained for describing photoelectron distributions affected by core-hole conduction electron interactions in metals. Chemical effects on core-hole lifetimes and hole-electron interactions are also reflected in conversion line shapes, as it is demonstrated in the case of $M_{4,5}$ conversion spectra from pertechnetate samples.

On the basis of the results of our analysis of conversion electron lines, the ICES method was applied for the determination of 3*p* and 3*d* lifetime broadenings in metallic technetium. Using an energy calibration procedure based on XPS measurements and core-level binding energies from previous XPS studies, the $E3$ nuclear transition energy was also computed from the measured conversion energies.

Besides providing some information to the quantitative application possibilities of the ICES method, the results suggest further application possibilities in resolution calibration of electron spectrometers and in determination of natural widths of several keV x-ray lines.

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