Investigation of technetium compounds by the method of conversion electron spectroscopy

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The chemical state and the electron structure of technetium and the surrounding atoms in nickel and copper pertechnetates, and in technetium-rhenium and technetium-copper alloys were determined by investigating the spectra of internal conversion electrons due to the $E3$ transition in ^{99m}Tc and of x-ray electrons. A detailed comparison was made and the experimental results were analyzed together with those of theoretical calculations of the electron structure and conversion probabilities carried out using the nonrelativistic and relativistic variants of the X_α scattered wave method. The example of technetium compounds is used in a discussion of the characteristics, capabilities, and probable ranges of applications of conversion spectroscopy of nuclear low-energy transitions as a method for investigating solids.

1. INTRODUCTION

Investigations of the influence of physicochemical conditions on the conversion process have started in the fifties. The results obtained so far have been discussed in several recent reviews.[1–4] Only a small part of the investigations has been devoted to changes in the spectra of internal conversion electrons. This has been due to the fairly poor energy resolution ($\gtrsim 100$ eV) of the instruments usually used in measurements.

Investigations of the spectra of conversion electrons due to the $E3$ transitions in ^{99m}Tc (Refs. 5–7) and ^{235m}U (Refs. 8 and 9) have shown that an improvement in the energy resolution of the spectra to $\lesssim 1$eV can provide valuable information on the structure of the chemical environment of the outer electron orbits which are deformed most by the chemical environment. This is due to the fact that the process of internal conversion is localized close to an isomer nucleus and is very selective in respect of the angular momentum of an electron relative to the isomer nucleus. For example, in the case of the $E3$ transition the conversion region dimensions are of the K-orbit size and the contributions of states with different angular momenta are of orders of magnitude which are in the ratio $s:p:d:f \sim 10^{-3}:1:0.1:10^{-3}$ (see Ref. 4).

We shall concentrate our attention on details of the electron structure of the valence band; we shall give examples of using conversion spectroscopy as a method for investigating solids.

2. EXPERIMENTS

The spectra were determined using an HP 5950A double-focusing electrostatic x-ray electron spectrometer made by Hewlett-Packard. The energy resolution of this spectrometer was constant throughout the investigated range of energies and it amounted to ≈ 1 eV. The measurement method was described in greater detail in Ref. 5.

Alloys were prepared by the method of electrolysis[7] on platinum substrates. The ratio of the components in the alloys was controlled by varying the amounts of $KTcO_4$, $HReO_4$, $CuSO_4$, and $NiSO_4$ added to the electrolyte. Technetium-copper alloys were also prepared by electrolysis on copper substrates. In this case the alloys were apparently formed as a result of diffusion of copper across a thin film of deposited technetium (see, for example, Ref. 10). We observed a diffusion of copper across technetium films of thicknesses up to several thousands of angstroms. This effect was not observed in the case of platinum.

Copper and nickel pertechnetates were prepared from technetium alloys deposited on platinum together with copper and nickel: these alloys were treated in hydrogen peroxide vapor at a temperature of ≈ 70°C for 30 min. The total mass of each of the sources prepared in this way was ~ 1 μg and the dimensions of the sources were about 1×5 mm.

The chemical composition of the sources was monitored, as before,[7] by x-ray electron spectroscopy (see Ref. 11). The composition of the alloys was found approximately from the relationships governing the intensities of the lines in the x-ray electron spectra.[5] According to Refs. 12 and 13, the Tc_xRe_{100-x} alloys formed solid solutions throughout the range $0 < x < 100$. It follows from the x-ray electron spectra (Figs. 1 and 2) that the binding energies ε of the technetium and rhenium lines agree with the values found from metallic technetium[5,11] and metallic rhenium.[14] The presence of surface contamination and slight oxidation of technetium and rhenium (within the limits of $\lesssim 5\%$) was observed in the sources.

We were unable to find any published data on technetium-copper alloys and the closest chemical analog of technetium, which is rhenium, does not in practice form solid solutions with copper.[13] It follows from the x-ray electron and the Cu $L_{2,3}VV$ Auger spectra that technetium in these alloys gives rise to two easily distinguishable states, whereas the chemical state of copper is metallic and oxidized approximately by 50% to Cu_2O (see Ref. 15). The amount of oxygen in the bulk of electrolytic copper is low,[16] but surface oxidation of copper in air is a fairly rapid process. For this reason the alloys of technetium with copper prepared in the form of thin films on substrates were oxidized. It was found that the degree of oxidation of these alloys correlated with the amount of copper. The atomic content of oxygen relative

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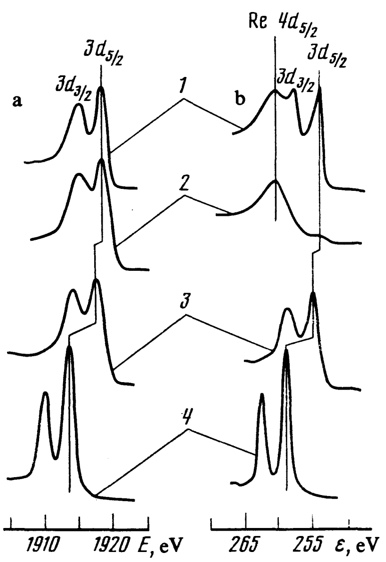

FIG. 1. Conversion (a) and x-ray (b) electron spectra in the region of the peaks of the 3d electrons of Tc in the following sources: 1) $Tc_{40}Re_{60}$; 2) Tc_5Re_{95}; 3) $Tc_{10}Cu_{90}$; 4) $Ni(TcO_4)_2 \cdot nH_2O$. In these and other figures the binding energy of electrons is denoted by ε and the kinetic energy of the conversion electrons is E.

to that of copper was ≈ 0.25. For the sake of simplicity, we omitted oxygen from the chemical formulas describing the compositions of technetium-copper alloys. The x-ray electron spectra of the sources in the form of nickel and copper pertechnetates agreed with the chemical state of the comparison compounds.[11]

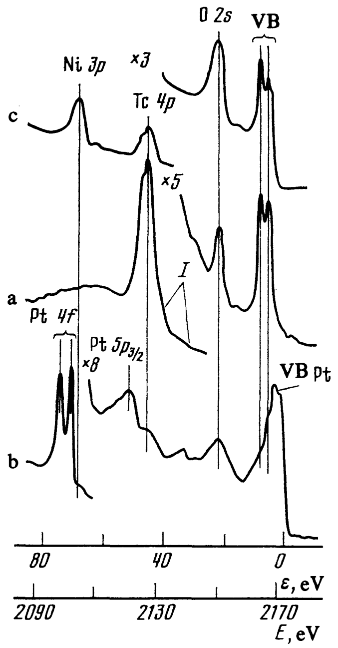

FIG. 2. Conversion (a) and x-ray (b) electron spectra in the region of the peaks of the outer electrons due to a $Ni(TcO_4)_2 \cdot nH_2O$ source on Pt and x-ray electron (c) of a standard $Ni(TcO_4)_2 \cdot nH_2O$ sample. The following notation is used in this figure: VB is the valence band; I are the Auger peaks of $L_3M_{4.5}M_{4.5}$ due to the conversion of ^{99m}Tc electrons with energies of about 140 and 142 keV.

3. RESULTS AND DISCUSSION

The conversion and x-ray electron spectra shown in Figs. 1–4 illustrate the properties and also identify some features of the information which can be obtained by the conversion method and not by x-ray electron spectroscopy.

1. The chemical shifts of the inner-electron lines of the investigated compounds (Fig. 1) correspond to the chemical shifts of the appropriate lines in the x-ray electron spectra, exactly as in Refs. 6 and 7.

2. The resolution of the lines in the conversion spectra is approximately equal to the resolution of the corresponding lines in the x-ray electron spectra (Figs. 1–4).

3. The high specific activity of ^{99m}Tc ensures in this case a higher absolute sensitivity of the conversion method when the amount of matter is small. In the overall x-ray electron spectrum (Fig. 3) of a source prepared by deposition of ≈ 10 ng of technetium on a copper substrate even the strongest 3d lines of technetium are barely detectable even under favorable background conditions. Under the same conditions the intensity of a set of the 3d lines in the conversion spectrum obtained for the same source is approximately 20 times higher (Fig. 3). When the amount of technetium is smaller (about 1 ng), it is not possible to separate the 3d lines in the x-ray electron spectrum from the background of Tc in an acceptable time. In the same case the conversion spectrum gives quite reliable information not only on the inner electron lines of technetium, but also on the structure of the weakest peaks in the spectrum representing the valence band (spectrum 9 in Fig. 4B).

4. The high selectivity in respect of the angular momenta and the localization of the conversion process are responsible for the high relative sensitivity of the conversion method in the case of specific electron orbitals (which have significant p- and d-electron densities near the technetium nuclei in the case of the $E3$ transition in ^{99m}Tc; see Ref. 7). The spectra of $Ni(TcO_4)_2 \cdot nH_2O$ in Fig. 2 demonstrate the importance of this property in the investigation of microscopic amounts of matter. In this case the x-ray electron spectrum in the outer-electron region (spectrum b), where the platinum and source-substance peaks strongly overlap, represents in practice only the electron structure of the platinum substrate [for comparison, Fig. 2 gives the x-ray electron spectrum of the bulk (comparison) sample of $Ni(TcO_4)_2 \cdot nH_2O$ (spectrum c)]. On the other hand, the selectivity of the conversion spectrum (denoted by a) reveals peaks representing the state of the technetium atoms in the source and the structure of this spectrum confirms the chemical state of technetium in the source in the form of pertechnetate, when allowance is made for the earlier information on the structure of the conversion spectra of pertechnetates.[6,7]

The high relative sensitivity of the conversion method ensures that the quality of the conversion spectra is practically unaffected by the presence of chemically inert impurities, surface contamination of the sources, and it is not influenced either by the substrate material.

5. The results of a quantitative analysis of the recorded conversion spectra are presented in Table I. For comparison,

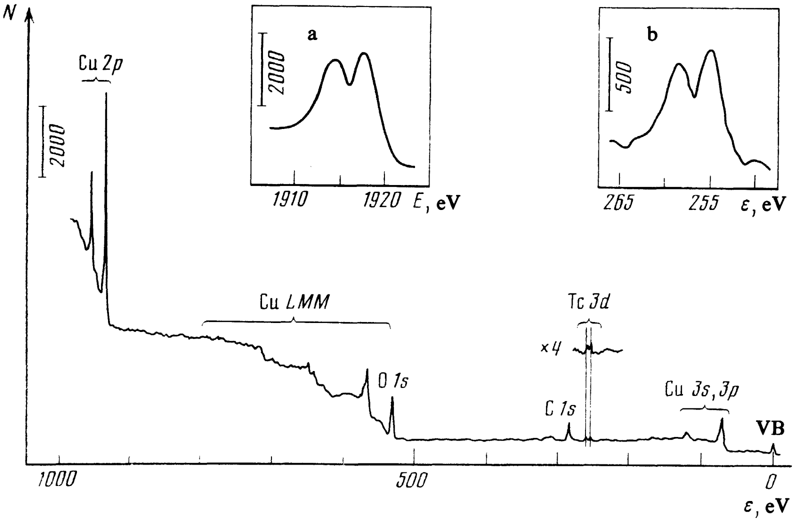

FIG. 3. Overall x-ray electron spectrum and parts of the conversion (a) and x-ray (b) electron spectra in the region of the $3d$ electron peaks of Tc in a source prepared by deposition of ≈ 10 ng of technetium on a copper substrate (the x-ray electron spectrum was recorded in a time interval five times longer than the inversion spectrum).

this table includes some experimental and calculated data obtained earlier. The relative probabilities of conversion are obtained after allowance for the influence of the inelastic scattering in the source material, by a method described in Refs. 5 and 7, on the relative intensities of the lines in the conversion spectrum. In accordance with the predictions obtained by calculation,[7,17,18] the experimental values of the relative probabilities of conversion for the inner $3p$ and $3d$ lines are constant within the limits of the experimental error. (Calculations reported in Refs. 17 and 18 overestimate the relative probability of conversion for the $3d$ electrons—see Ref. 7.) The conversion spectra of $Ni(TcO_4)_2 \cdot nH_2O$ (see Figs. 2 and 4A) and of $Cu(TcO_4)_2 \cdot mH_2O$ are similar to the spectra obtained earlier[6,7] for NH_4TcO_4 and $KTcO_4$. This similarity and the data of Table I confirmed the conclusion reached in Ref. 7 that the cation has little influence on the electron density near the technetium nuclei.

According to the data obtained earlier[6,7] and in the present study (Table I, Fig. 4A), the calculated intensities of the conversion lines due to the outer electron states in $TcBr_6^{2-}$ and TcO_4^- are somewhat underestimated compared with the experimental results. This situation has already been considered earlier.[7] It is assumed that the potential acting on an electron in a real anion differs greatly from the muffin-tin potential, i.e., there are potential troughs between the anion atoms along which the electrons move relatively easily from atom to atom.

Our results for Tc_xRe_{100-x} with $x = 5$, 40, and 50 (Fig. 1 and Table I) indicate that the state of technetium in these alloys is clearly analogous to technetium in the metallic state.

In the case of $Tc_{10}Cu_{90}$ the relative probabilities of conversion are lower than for Tc_xRe_{100-x} (Table I) and this is true both of the valence electrons and of the $4p$ electrons. This reduction may be due to a reduction in the absolute probabilities of conversion involving the outer electrons, and a reduction of these probabilities in the case of the inner $3p$ and $3d$ electrons. The results can be improved by suitable

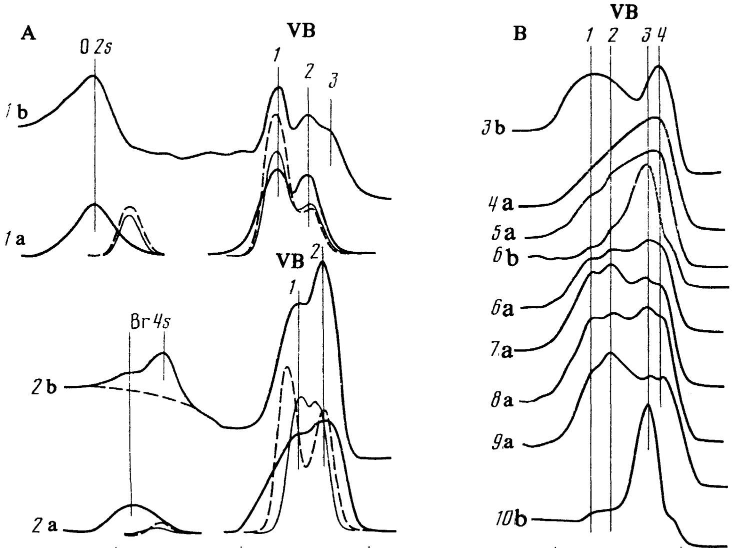

FIG. 4. A) Comparison of the experimental conversion (a) and x-ray (b) spectra of standard samples in the region of the peaks of the outer electrons [thick curve; 1) $Ni[TcO_4]_2 \cdot nH_2O$; 2) $(NH_4)_2TcBr_6$ data taken from Ref. 7] with the results of theoretical calculations of the conversion spectra of TcO_4^- and $TcBr_6^{2-}$ ions (thin curves represent our results and the dashed curves are taken from Ref. 18). B) Structure of the valence band manifested in the conversion (a) and x-ray (b) electron spectra of the following sources and samples: 3) TcO_2; 4) Tc_{metal}; 5) $Tc_{50}Cu_{50}$; 6) $Tc_{20}Cu_{80}$; 7) $Tc_{10}Cu_{90}$; 8) about 10 ng of Tc on Cu; 9) about 1 ng of Tc on Cu; 10) Cu_2O.

TABLE I.

	Intensities relative to $3p_{3/2}(\times 100)$				
	$3p_{1/2}$	$3d$	$4p$	O $2s$	valence band
Tc_xRe_{100-x} (exp., our results)	57,2±1,0	47,8±0,5	25,5±0,7		4,2±0,2
Tc_{metal} (exp., Ref. 5)	57,0±1,8	47,2±1,0	26,1±2,3		4,4±0,5
Tc_{metal} (theory, Ref. 17)	56,3	53,6	24,4		4,36
$Tc_{10}Cu_{90}$ (exp., our results)	57,3±0,5	47,1±0,5	22,1±0,5		3,5±0,2
$Ni(TcO_4)_2 \cdot nH_2O$ (exp., our results)	56,1±0,8	48,4±0,5	23,6±0,9	1,5±0,2	3,4±0,2
$Cu(TcO_4)_2 \cdot mH_2O$ (exp., our results)	56,6±1,0	47,8±1,6	24,5±1,5	1,5±0,2	3,7±0,2
$KTcO_4$ (exp., Ref. 7)	56,7±1,5	47,8±1,4	23,7±1,2	1,8±0,3	3,5±0,3
NH_4TcO_4 (exp., Ref. 6)	56,0±2	47,4±2,8	23,8±1,7	2,2±0,8	3,8±0,5
TcO_4^- (theory, Ref. 7)	56,7	47,4	25,5	0,76	2,71
TcO_4^- (theory, Ref. 18)	56,3	53,7	25,2	0,92	3,38

measurements of changes in the decay constant, i.e., from the conversion probability integrated over the spectrum. It should be noted that the conversion probability for electrons in the valence band of Tc_xRe_{100-x} solid solutions and of metallic technetium is clearly higher than in the case of pertechnetates, which is in agreement with the results of calculations given in Refs. 17 and 18.

6. The good resolution of the conversion spectra in the region of the valence band makes it possible to carry out a detailed comparison of the experimental results with the data obtained by calculations in Refs. 7 and 18, carried out using the relativistic[19] and nonrelativistic variants of the X_α scattered wave method. A similar, but more detailed than in Ref. 7, comparison was made by us for $(NH_4)_2TcBr_6$.

Tables II and III give the numerical results of a theoretical calculation of the electron structure and of the conversion probabilities for the TcO_4^- and $TcBr_6^{2-}$ anions. Classification of the molecular orbitals is based on the irreducible representations of the double groups $T'd$ and $O'h$ (Ref. 20). The colums of these two tables give the following information: the first column gives the type of orbital in the relativistic and nonrelativistic (the latter in parentheses) approximations and the occupation numbers (n_l); the second lists the theoretical values of the binding energies ($\varepsilon_{\text{theor}}$); the third gives the partial charge in a technetium sphere (Q_{Tc}); the fourth lists the partial charges in the technetium sphere in accordance with the nature of the orbital and total momentum (l); the fifth column provides the relative probabilities of the conversion process (w_e). In these calculations it is assumed that the inner electrons of technetium, oxygen, and bromine are in the atomic states in the appropriate spheres.[19] A graphical comparison of the experimental spectra with the results of theoretical calculations is made in Fig. 4A. The theoretical spectra are obtained by summation of the individual spectral components of w_e (Tables II and III) represented by peaks with Gaussian profiles and a total width at half-amplitude amounting to 2 eV for TcO_4^- and 1.5 eV for $TcBr_6^{2-}$. The spectrum of inelastically scattered electrons is subtracted from the experimental spectra. The areas under the peaks of the experimental and theoretical conversion spectra are normalized to the intensities of the $3p_{3/2}$ lines of technetium in the appropriate spectra. The Arabic numbers in Fig. 4A denote the valence band maxima observed in the spectra. The maximum 3 present in the x-ray electron spectrum of $Ni(TcO_4)_2 \cdot nH_2O$ does not appear in the corresponding conversion spectrum. It follows that this maximum is due to the valence electrons of nickel, which do not form molecular orbitals with significant p- or d-electron densities near the technetium nuclei. The theoretical spectra for TcO_4^- and $TcBr_6^{2-}$ are in qualitative agreement with the

TABLE II. Results of calculations for TcO_4^- anion

State, n_l	$\varepsilon_{\text{theor}}$, eV	Q_{Tc}, %	l, %	w_e, 0/00
$(1t_1)$ γ_8, 4	8,77	0,87	$35{,}5f_{5/2}$; $64{,}0f_{7/2}$; $0{,}3d_{5/2}$; $0{,}2p_{3/2}$	0,00
γ_6, 2	8,79	0,87	$0{,}7s_{1/2}$; $59{,}6f_{5/2}$; $39{,}7f_{7/2}$	0,00
$(4t_2)$ γ_8, 4	9,11	4,8	$54{,}3p_{3/2}$; $29{,}0d_{3/2}$; $16{,}7d_{5/2}$	2,42
γ_7, 2	9,19	4,7	$57{,}9p_{1/2}$; $42{,}1d_{5/2}$	1,30
$(2a_1)$ γ_6, 2	9,49	9,2	$88{,}3s_{1/2}$; $4{,}8f_{5/2}$; $6{,}9f_{7/2}$	0,00
$(1e)$ γ_8, 4	11,66	35,7	$18{,}7d_{3/2}$; $81{,}3d_{5/2}$	3,10
$(3t_2)$ γ_7, 2	11,84	35,5	$0{,}1p_{1/2}$; $99{,}4d_{5/2}$; $0{,}5f_{7/2}$	1,54
γ_8, 4	11,91	37,4	$82{,}5d_{3/2}$; $17{,}0d_{5/2}$; $0{,}3f_{5/2}$; $0{,}2f_{7/2}$	3,21
$(2t_2)$ γ_8, 4	23,55	6,7	$29{,}6p_{3/2}$; $40{,}8d_{3/2}$; $26{,}3d_{5/2}$; $2{,}1f_{5/2}$; $1{,}2f_{7/2}$	2,21
γ_7, 2	23,62	6,4	$28{,}1p_{1/2}$; $68{,}4d_{5/2}$; $3{,}5f_{7/2}$	1,06
$(1a_1)$ γ_6, 2	23,78	3,9	$79{,}1s_{1/2}$; $9{,}0f_{5/2}$; $11{,}9f_{7/2}$	0,00
$(1t_2)$ γ_8, 4	47,47	96,1	$100{,}0p_{3/2}$	69,35
γ_7, 2	50,41	96,9	$100{,}0p_{1/2}$	39,88
$4s_{1/2}$, 2	73,82			0,05
$3d_{5/2}$, 6	251,30			122,42
$3d_{3/2}$, 4	255,12			81,04
$3p_{3/2}$, 4	412,06			429,09
$3p_{1/2}$, 2	431,87			243,16
$3s_{1/2}$, 2	520,15			0,17
				$\Sigma = 1000{,}00$

TABLE III. Results of calculations for $TcBe_6^{2-}$ anion

State, n_l		ε_{theor}, eV	Q_{Tc}, %	l, %			w_e, 0/00
$(2t_{2g})$	γ_{8g}, 3	6,84	19,4	$65,3d_{3/2}$;	$34,7d_{5/2}$		1,20
$(1t_{1g})$	γ_{8g}, 4	6,96	45,2	$50,5d_{3/2}$;	$49,5d_{5/2}$		3,70
	γ_{6g}, 2	7,14	0,09	$100,0s_{1/2}$			0,00
$(4t_{1u})$	γ_{8u}, 4	6,73	2,2	$64,6p_{3/2}$;	$24,7f_{5/2}$;	$10,7f_{7/2}$	0,59
	γ_{6u}, 2	7,27	3,3	$75,7p_{1/2}$;	$24,3f_{7/2}$		0,54
$(1t_{2u})$	γ_{7u}, 2	7,19	0,24	$57,0f_{5/2}$;	$43,0f_{7/2}$		0,08
	γ_{8u}, 4	7,40	0,4	$45,2p_{3/2}$;	$13,4f_{5/2}$;	$41,4f_{7/2}$	0,00
$(3t_{1u})$	γ_{6u}, 2	8,14	2,6	$100,0p_{1/2}$			0,56
	γ_{8u}, 4	8,32	2,9	$98,7p_{3/2}$;	$0,1f_{5/2}$;	$1,2f_{7/2}$	1,23
$(2e_g)$	γ_{8g}, 4	8,65	40,3	$79,1d_{3/2}$;	$20,9d_{5/2}$		2,94
$(1t_{2g})$	γ_{7g}, 2	8,63	20,5	$100,0d_{5/2}$			0,74
	γ_{8g}, 4	8,89	19,4	$9,4d_{3/2}$;	$90,6d_{5/2}$		1,38
$(2a_{1g})$	γ_{6g}, 2	8,97	5,0	$100,0s_{1/2}$			0,00
$(1e_g)$	γ_{8g}, 4	20,07	1,6	$40,6d_{3/2}$;	$59,4d_{5/2}$		0,05
$(2t_{1u})$	γ_{8u}, 4	20,09	0,35	$82,3p_{3/2}$;	$11,3f_{5/2}$;	$6,4f_{7/2}$	0,15
	γ_{6u}, 2	20,10	0,35	$82,4p_{1/2}$;	$17,6f_{7/2}$		0,07
$(1a_{1g})$	γ_{6g}, 2	20,46	1,5	$100,0s_{1/2}$			0,00
$(1t_{1u})$	γ_{8u}, 4	44,48	99,0	$100,0p_{3/2}$			67,97
	γ_{6u}, 2	47,39	99,2	$100,0p_{1/2}$			39,04
	$4s_{1/2}$, 2	72,52					0,04
	$3d_{5/2}$, 6	248,0					123,41
	$3d_{3/2}$, 4	251,8					81,78
	$3p_{3/2}$, 4	408,8					431,08
	$3p_{1/2}$, 2	428,6					243,28
	$3s_{1/2}$, 2	516,9					0,17
							$\Sigma=1000,00$

experimental spectra. However, a detailed analysis shows that the experimental and theoretical conversion spectra yield very different values of the ratio of the intensities of the maxima 2 and 1. A completely relativistic calculation gives in both cases a better approximation to the experimental results than the calculations reported in Ref. 18.

A comparison of the results of calculations reported by Hartmann *et al.* (see Table II in Ref. 18) with those of completely relativistic calculations (Table II and III in the present study) reveals the following. On the whole, the agreement between the results of these calculations of the electron structure of clusters in the case of TcO_4^- is good, but our results for the γ_7 and γ_8 orbitals, corresponding to the $4t_2$ orbital in the nonrelativistic approximation, yield a composition of the partial charge in a technetium sphere deformed from that obtained in Ref. 18. There are similar differences in the case of $TcBr_6^{2-}$ for the γ_{6g} and γ_{8g} orbitals, which correspond to the $1t_{1g}$ orbitals in the nonrelativistic approximation. In both cases the completely relativistic variant of the calculations gives rise to an additional *d*-electron density, which makes a significant and further contribution to the conversion for the valence electrons forming the maximum 2 in Fig. 4A. Since both variants of the calculations of the electron structure of the TcO_4^- and $TcBr_6^{2-}$ clusters are made using the same parameters of the clusters and the same initial asumptions, it follows that the difference between the results should be attributed to the influence of the relativistic effects. Additionally, the higher relative probabilities of conversion for the *d* electrons give rise to higher intensities of the maximum 1 (see Fig. 4A) compared with the maximum 2 in the theoretical spectra of Ref. 18.

7. Figure 4B illustrates the potential usefulness of the conversion method in the case of an analysis of the states of technetium in its alloys with copper. The conversion spectra demonstrate a strong dependence of the nature of the spectra on the composition of the alloys. A relative reduction in the technetium content increases considerably the intensities of the maxima 1 and 2. The x-ray electron spectra of the valence band are affected only slightly; the peaks 1 and 2 are very noticeable only in the case of $Tc_{20}Cu_{80}$ (Fig. 4B). This can be explained as follows.

At high technetium concentrations ($>50\%$) the alloys are clearly eutectic mixtures. In this case the spectra represent the metallic state of technetium. A reduction in the technetium concentration to 10% results in a gradual replacement of the eutectic with a certain phase which clearly has a definite stoichiometry. This is indicated by the spectra of the 3*d* electrons of technetium. A comparison of the conversion and x-ray electron spectra of TcO_2 and Cu_2O, as well as an allowance for the properties of the conversion process and the usual—in the formation of chemical bonds with metal—behavior of the 2*p* electrons of oxygen (see, for example, Ref. 21), yield the following conclusions. The maxima 3 and 4 are formed mainly by the valence electrons of technetium and copper, whereas the maxima 1 and 2 are mainly due to the valence electrons of technetium and oxygen. The phase obtained in the case of $Tc_{10}Cu_{90}$ is clearly a ternary system Cu–Tc–O which is a chemical compound.

4. SUMMARY OF RESULTS. CHARACTERISTICS AND POTENTIAL APPLICATIONS OF CONVERSION SPECTROSCOPY OF LOW-ENERGY NUCLEAR TRANSITIONS

A combined investigation of the conversion and x-ray electron spectra of various materials containing technetium, and a comparison with the data of the available calculations have made it possible to obtain information on the electron structure and chemical state of both technetium and these materials and have revealed important properties of the conversion spectra. A good quantitative agreement has been obtained overall between the experimental and calculated results. However, a detailed comparison shows that a better agreement with the experimental data is obtained when the totally relativistic variant of the calculations is used rather than the approach used in Ref. 18. On the other hand, the experimental results indicate much higher probabilities of conversion for the outer electrons participating in chemical bonds than do the calculations. The theoretical conversion spectra yield the ratio of the intensities of the valence band peaks which differs greatly from the ratio found from the experimental spectra. It follows that the real electron structure differs significantly from that obtained by calculation. The conversion method is highly sensitive to details of the behavior of the electron density and, alongside the x-ray electron and x-ray spectroscopy methods, will be useful in verifying the models of the structure of matter employed in calculations.

We shall now mention the principal properties and characteristics of the conversion method which determine its potential applications. The most important feature of the method is the sensitivity to the chemical state of a given type of atom and the main characteristics, which make it possible to obtain basically new information on the electron structure of matter, are the localization of the conversion process in the direct vicinity of the isomer nuclei[4,22] and clear separation of the contribution made to the conversion spectrum by states with a fixed angular momentum relative to the isomer nuclei.[4] The following properties and features determine the methodological capabilities of the conversion spectroscopy method: the high absolute sensitivity to the atoms of isomers with a high specific activity, governed by the isomer half-decay time; the high relative sensitivity; the high resolution; feasibility of investigating the properties of surfaces (this is related, as in the case of x-ray electron spectroscopy, to the low energy of the conversion electrons); the feasibility of using the tagged atom (tracer) techniques. This last feature of the conversion method provides, in principle, an opportunity to tag atoms in just one of the states in compounds containing atoms of a given element in different chemical states. On the other hand, the sensitivity of the method in studying surface atoms can be enhanced by tagging the surface atoms.

The conversion method is clearly most valuable in studies of the properties of surfaces, particularly catalytic and corrosion properties, and also in investigations of the chemical state of the elements, the presence of which in small amounts in media is responsible for their important physicochemical properties. The conversion spectra of gaseous samples are of special interest because the lines due to the outer electrons of such samples have small half-widths.

The conversion method with a sufficiently high resolution has been used so far to study only the compounds of Tc and U. The range of elements which form compounds that can be investigated by the conversion method will become wider after a number of methodological problems are solved, the most important of which is extension of the range of the measured energies by electrostatic spectrometers used at present in x-ray electron spectroscopy while retaining the absolute resolution of the spectra already achieved. Electron spectrometers with parameters close to those required are already available.[1]

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[1] O. Dragoun, Adv. Electron. Electron Phys. **60**, 1 (1983).
[2] K. P. Dostal, M. Nagel, and D. Pabst, Z. Naturforsch. Teil A **32**, 345 (1977).
[3] K. V. Makaryunas, Izv. Akad. Nauk SSSR Ser. Fiz. **47**, 18 (1983).
[4] D. P. Grechukhin and A. A. Soldatov, Issledovanie konversionnogo protsessa v svyazi s effektami khimicheskogo okruzheniya atoma: obzor (Investigation of the Conversion Process in Relation to the Effects of the Chemical Environment of an Atom: Review), Institute of Atomic Energy, Moscow, 1982; Vopr. At. Nauki Tekh. Ser. Yad. Konstanty No. 2(56), 36 (1984); Yad. Fiz. **38**, 1397 (1983), **23**, 273 (1976) [Sov. J. Nucl. Phys. **38**, 849 (1983), **23**, 143 (1976)]; Preprint No. 3174, Institute of Atomic Energy, Moscow, 1979.
[5] V. N. Gerasimov, A. G. Zelenkov, V. M. Kulakov, V. A. Pchelin, A. A. Soldatov, V. A. Stepanchikov, and L. V. Chistyakov, Yad. Fiz. **34**, 3 (1981) [Sov. J. Nucl. Phys. **34**, 1 (1981)].
[6] V. N. Gerasimov, A. G. Zelenkov, V. M. Kulakov, V. A. Pchelin, M. V. Sokolovskaya, A. A. Soldatov, and L. V. Chistyakov, Zh. Eksp. Teor. Fiz. **82**, 362 (1982) [Sov. Phys. JETP **55**, 205 (1982)].
[7] V. N. Gerasimov, A. G. Zelenkov, V. M. Kulakov, V. A. Pchelin, M. V. Sokolovskaya, A. A. Soldatov, and L. V. Chistyakov, Zh. Eksp. Teor. Fiz. **86**, 1169 (1984) [Sov. Phys. JETP **59**, 683 (1984)].
[8] V. I. Zhudov, A. G. Zelenkov, V. M. Kulakov, V. I. Mostovoĭ, and B. V. Odinov, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 549 (1979) [JETP Lett. **30**, 516 (1979)].
[9] D. P. Grechukhin, V. I. Zhudov, A. G. Zelenkov, V. M. Kulakov, B. V. Odinov, A. A. Soldatov, and Yu. A. Teterin, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 627 (1980) [JETP Lett. **31**, 592 (1980)].
[10] R. W. Balluffi and J. M. Blakely, Thin Solid Films **25**, 363 (1975).
[11] V. N. Gerasimov, S. V. Kryuchkov, A. F. Kuzina, V. M. Kulakov, S. V. Pirozhkov, and V. I. Spitsyn, Dokl. Akad. Nauk SSSR **266**, 148 (1982).
[12] A. Brenner, Plating **52**, 1249 (1965).
[13] F. A. Shunk, Constants of Binary Alloys, Second Supplement, McGraw-Hill, New York, 1969 (Russ. transl., Metallurgiya, M., 1973).
[14] R. Nyholm, A. Berndtsson, and N. Martensson, J. Phys. C **13**, L1091 (1980).
[15] Kh. M. Minachev, G. V. Antoshin, and E. S. Shpiro, Fotoeléktronnaya spektroskopiya i ee primenenie v katalize (Photoelectron Spectroscopy and Its Applications in Catalysis), Nauka, M., 1981, p. 69.
[16] V. A. Lamb and D. R. Valentine, Plating **53**, 86 (1966).
[17] E. Hartmann and G. Seifert, Phys. Status Solidi B **100**, 589 (1980).
[18] E. Hartmann, R. Der, and M. Nagel, Z. Phys. A **290**, 349 (1979).
[19] A. A. Soldatov, Preprint No. 3916, Institute of Atomic Energy, Moscow, 1983.
[20] V. Heine, Group Theory in Quantum Mechanics, Pergamon Press, London, 1960 (Russ. transl., IL, M., 1963).
[21] V. V. Nemoshkalenko and V. G. Aleshin, Élektronnaya spektroskopiya kristallov (Electron Spectroscopy of Crystals), Naukova Dumka, Kiev, 1976, p. 255.
[22] I. M. Band, L. A. Sliv, and M. B. Trzhaskovskaya, Nucl. Phys. A **156**, 170 (1970)

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