TECHNETIUM METAL AND PYROMETALLURGICALLY FORMED SEDIMENTS STUDY AND SPECIATION BY Tc-NMR AND EXAFS / XANES

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Abstract : EXAFS and NMR are being developed with respect to study and speciation of technetium-99 in course of pyrometallurgical reprocessing of spent nuclear fuel. Based on the set of standards including technetium metal, different techentium halogenides, oxohalogenides, oxydes and pyrometallurgically formed sediments, Tc chemical forms responsible for Tc accumulation in fused salts, deposits or gas-off depending on the applied reprocessing conditions are studying by means of NMR and EXAFS. NMR spectrum of Tc metal powder obtained by FT of a free induction decay accumulated after excitation of the spin system by a sequence of high frequency pulses (0.8 ìs) with a dead time of 5.4 ìs and a repetition time of 1 ìs, provided with Knight shift K(ppm) = 7305 - 1.52 ^{x} T; $v_Q(^{99}Tc)$ = 230 kHz at 293 K , $C_Q(^{99}Tc)$ = 5.52 MHz. EXAF spectra provided with excellent evidence for Tc(IV) halogenides, but need further development for lower oxidation states of technetium.

Introduction : EXAFS and NMR are promising methods to enable us with speciation of radioactive nuclides. It is important to use them for Tc speciation in pyrometallurgy which is now considered as the most probable alternative approach to reprocessing of spent nuclear fuel. Pyrometallurgy of uranium and plutonium in chloride and fluoride fused salts are now intensively studied while little attention is given to long lived fission product technetium which is one of the hazardous nuclear wastes. During pyrometallurgical spent fuel reprocessing, technetium can remain in the fused salt or enter (depending on the applied temperatures, reagents and potentials) either the sedimented phase contaminating Pu enriched phase, or electrodeposited U phase (Scheme 1). Neither in sediment nor in deposit Tc phase could be detected by means of X-ray diffraction, Tc phase being finely dispersed and X-ray amorphous. It is therefor very important to develop some other methods of analyses like EXAFS and NMR applicable to Tc speciation in such samples.

Our preliminary results show that under such conditions Tc can also form several oxydes, oxychlorides and chlorides of different but rather high volatility, turning on an important polluting risk allied to gas-off .

The data on EXAF and NMR spectra of technetium being fragmentary and not presenting the whole of the species possible in the pyrometallurgy conditions, it is of high importance to carry synthetic work to supply a large set of technetium compounds in the closed containers which will meet the security and quality demands, radioactivity level, special requirements on sample size, thickness, sample homogeneity.

Some EXAFS measurements of technetium solutions applicable in some content to pyrometallurgcal treatment of spent nuclear fuel were presented earlier by [1, 2]. It provided with EXAF data on technetium(IV) hexachloride in HCl solution. Recent studies however has given some indication on the presence of unknown Tc chloride complex [3]

Tc metal and its binary alloys with vanadium have been studied earlier by ^{99}Tc NMR at ambient temperature [4, 5, 6]. In these early works, the measurements were made in relatively low magnetic fields (B$_0$ 1,4 T) in the differential passing mode with field sweep, which made difficult the measurements of the anisotropic Knight shift (K$_{an}$). Moreover, the reported values of isotropic Knight shift (K) for metal Tc varied from K= 6100 ppm in [4, 5] to K= 7150 ppm and K$_{an}$= 1160 ppm in [6].

Experimental : In this work EXAFS measurements are made at Radiochemical Hutch of ROBL/ ESRF: beamsize of 3 x 20 mm^2, integrated flux at sample 6 x 1011 /s 200mA@ 20kEV, spectral range 5 - 35 keV; 2/3 filling mode. Beam line control carried out with VME,SUN workstation, SPEC Hot cells are used for sample positioning.

[99]Tc NMR spectra of Tc metal powder at 120-400 K, technetium foil and some preliminary results on the K(^{99}Tc) shifts in the alloy samples were recorded on a Bruker MSL-300 radiospectrometer in 7.04T magnetic field at 67.55 MHz resonance frequency.

Spectra NMR were obtained by FT of a free induction decay accumulated after excitation of the spin system by a sequence of high frequency pulses (0.8 ìs) with a dead time of 5.4 ìs and a repetition time of 1 ìs. The Knight shifts were measured relative to the external standard 0.1M KTcO$_4$ aqueous solution.

Chemical preparations: All reagents were chemically pure grade. Technetium was purchased as NH$_4$TcO$_4$ from Amersham Co. and as KTcO$_4$ from V/O ISOTOP, RF and converted to HTcO$_4$ by cation exchange. N(CH$_3$)$_4$TcO$_4$ was prepared as discribed in [7]Tc metal was prepared by reduction of tetramethylammonium pertechnetate N(CH$_3$)$_4$TcO$_4$ (of 99.9% purity) in a flow of non-explosive gas mixture 6% H$_2$ in Ar in a quartz tube at 1150 K. Samples were cooled, crashed and the 80-150 ìm fraction was sieved of for NMR measurements. Same method was used for preparation of the dispersed metal on metal oxide supports MgO, Al$_2$O$_3$, modified for evaporation of NH$_4$TcO$_4$ at the later surface. To improve the resolution and accumulation NMR mode minimizing the electric contacts, some technetium metal samples were dispersed in dodecane : apiezon (20 : 1) mixture and then air-dried.

Tc halogenides and oxydes were prepared as discribed in [8, 9]. Reference technetium compounds prepared for EXAFS study : chlorides (M$_2$TcCl$_6$, M = Li, Na, K, R$_4$N); fluorides, (M$_2$TcF$_6$, M= H, Na, K); bromides (M = Na, K, R$_4$N); oxides TcO$_2$, Tc$_4$O$_5$ and pertechnetates MTcO$_4$ (M = Na, K, Cs,); Samples of simulated pyrometallurgically reprocessed nuclear fuel (to be prepared): Technetim hexachlorides in fused salts (chlorides and fluorides); Tc sublimated fraction; Tc precipitated/deposit fraction (*all with Tc-99 as the only radionuclide*)

Results and discussion: The ^{99}Tc-NMR spectrum of polycrystalline metallic Tc comprises 8 symmetrically arranged satellites and the central component whose shape is governed by the Knight shift anisotropy (Fig 2).

The distance in KHz between the first inner satellites is the lowest frequency of a quadruple transition í$_Q$. The line width of the central component at half-maximum was ~ 22 kHz at 293 K thus having masked the effects of shift-anisotropy on the lineshape of the central transition (-1/2 +1/2).

At 400 K the line width is reduced and shows the axially – symmetric lineshape with K - K = -809 ± 30 ppm.

Fig. 2 presents the temperature dependence of the isotropic Knight shift for technetium metal powder, and Fig. 3 presents the temperature independence of the v_Q for the same sample. This study provided with K(ppm) = 7305 - 1.52 ^{x} T; R^2 = 0.99. Experimental v_Q(^{99}Tc) is 230 kHz at 293 K which gives C$_Q$(^{99}Tc) = 5.52 MHz. The latter is related to electric field gradient EFG (q^{exp}) by the equation: q^{exp} [cm^{-3}] = 2.873*10^{22} C$_Q$[MHz]/Q[barn] =52.86*10^{22} cm^{-3} , where Q = 0.3 barn.

In general, the total EFG at a nuclear site in a noncubic metal results from the addition of two EFG parts, one being due to the lattice of the ionic core (enhanced by the Sternheimer antishielding effect) and the other being due to the non-s-character of the conducting electrons:

$$q^{exp} = (1-ã)q^{lat} + q^{el} .$$

In case of Tc, the contribution arising from the ionic core lattice may be interpolated from de Wette's [10] results for á = c/a = 1.604. We find that (1-ã)q^{lat} = 27.57*10^{22} cm^{-3} (at ã = -5 [11]). This value is 52% of the experimental value obtained in the present work. This proportion is typical of the most metals in which the (1-ã)q^{lat} contribution is ussually lower (in magnitude) than the observed one.

At the ^{99}Tc-NMR spectrum of Tc metal foil of 20 μm (Fig. 5), the central component is very close to its position in Tc metal powder sample, but the 8 satellites are missed or not clear due to highly defected crystal cell caused by mutual consecutive mechanic treatments. NMR and EXAFS studies of dispersed Tc (supported on oxide matrix of MgO and Al$_2$O$_3$) and of Tc-Ru and Tc-Rh alloys are in progress. NMR spectrum of the sample, sedimented from K$_2$TcCl$_6$ in NaCl-KCl melt at 550°C under reducing conditions formed by Ar-1%H$_2$ bubbling, gave evidence for some metal state (9884 ppm) but also some to 30% of Tc(VII) (31 ppm).

Three main aspects under consideration with respect to EXAFS/XANES studies are the following: 1) the ligand influence on the technetium EXAF spectra within the same Tc oxidation state (F, Cl, Br, I and OH, H$_2$O being the ligands of interest with respect to pyrometallurgy as a reprocessing method), 2) the oxidation state including the lower and mixed oxidation states as well as Tc cluster formation on the technetium EXAF spectra 3) cations on the technetium EXAF spectrum within the same Tc oxidation state (Li, Na, K, Rb, Cs, Me$_4$N, Et$_4$N, Pr$_4$N, Bu$_4$N could be the cations of interest , while TcO$_4^-$ and TcHal$_6^{-2}$ would be the anions under study (some preliminary results are given in Fig. 6 and 7).

Tc K-edge k^3-weighted EXAFS and corresponding Fourier transform of the sample of standard Tc(IV) halogenide (Me$_4$N)$_2$TcBr$_6$ is present at Fig. 6. It resulted in the following EXAFS structural parameters:

Tc-Br N=5.8(2) ; R=2.51(2) Å ; σ^2 = 0.0040 Å^2 ; ΔE$_0$= -16.9(5) eV

Six halogenide atoms and the distance found correspond well to the same parameters known for similar compounds based on X-ray monocrystal analyses.

Tc K-edge k^3-weighted EXAFS and corresponding Fourier transform of the standard Tc(2,5+) halogenide sample $K_3Tc_2Cl_8$ is present in Fig. 7. The first coordination sphere of Tc in this compond includes one Tc atom and four Cl atoms. EXAFS structural parameters for $K_3Tc_2Cl_8$ (in such preliminary approximation) resulted in the following values:
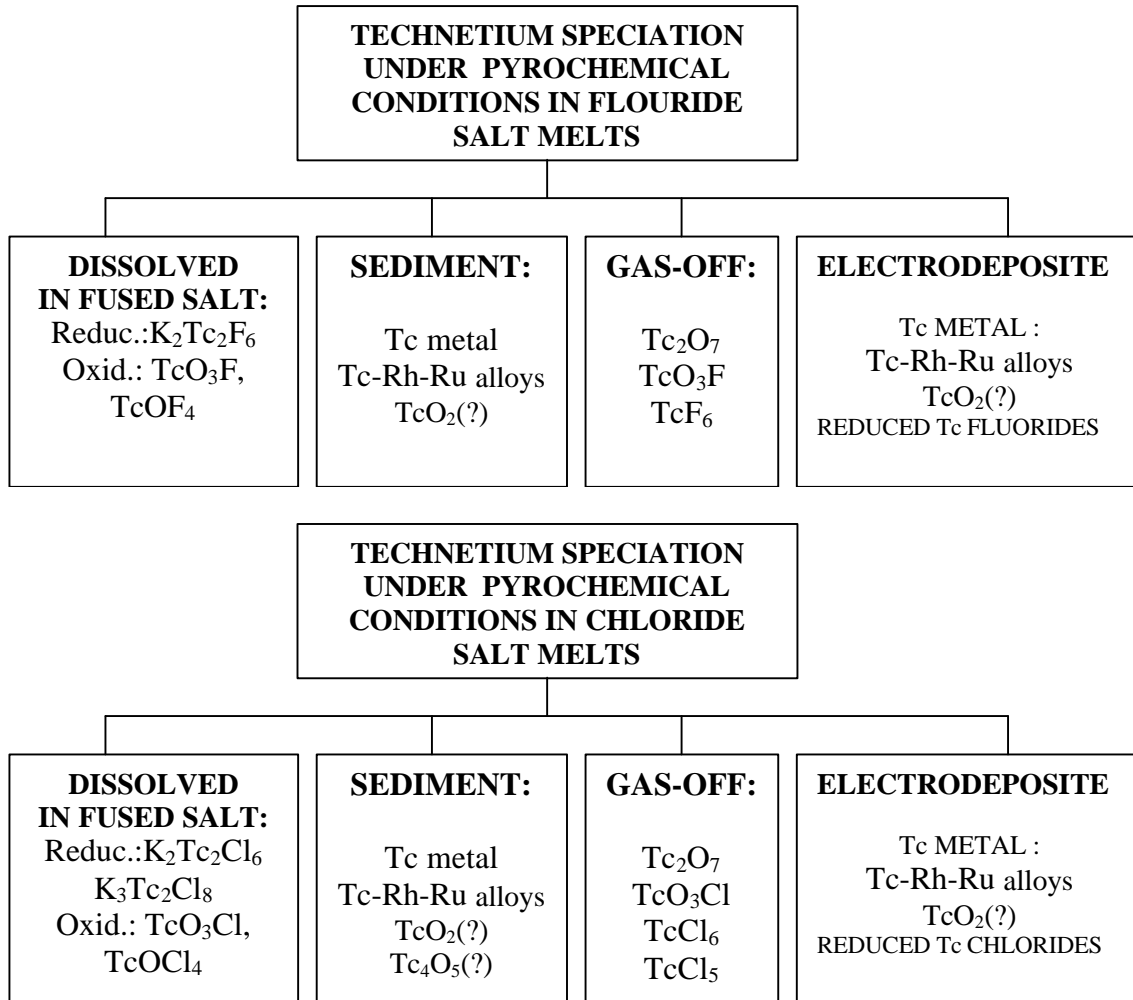
Tc-Tc N=1.6(3)   R=2.20(2) Å σ^2=0.0069 Å^2 $\Delta E0$=-1.1(9) eV
Tc-Cl   N=2.2(4)   R=2.46(2) Å σ^2=0.0107 Å^2

The overestimation of Tc-Tc intervention is evidently due to neglection of the four chlorine atoms bounded to the second technetium atom. This correction of the model will be made in the nearest future.

The results show excellent agreement in case of octahedral Tc(IV) bromide while for Tc cluster compound an important difference between the experimental and the fit suppose that some more chloride atoms but not only the first coordination sphere chlorides are influencing the EXAF spectrum.

SCHEME 1

Possible Tc species
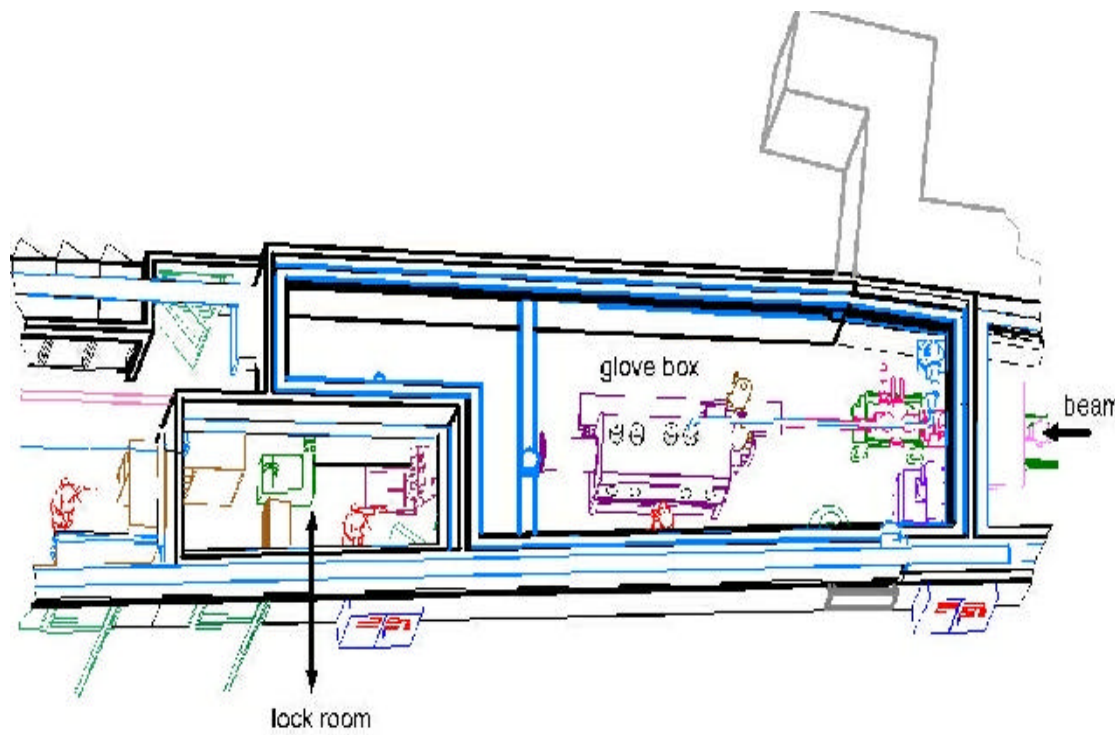## in PYROCHEMICAL REPROCESSING
of spent nuclear fuel

TECHNETIUM SPECIATION UNDER PYROCHEMICAL CONDITIONS IN FLOURIDE SALT MELTS

DISSOLVED IN FUSED SALT:	**SEDIMENT:**	**GAS-OFF:**	**ELECTRODEPOSITE**
Reduc.:$K_2Tc_2F_6$ Oxid.: TcO_3F, $TcOF_4$	Tc metal Tc-Rh-Ru alloys TcO_2(?)	Tc_2O_7 TcO_3F TcF_6	Tc METAL : Tc-Rh-Ru alloys TcO_2(?) REDUCED Tc FLUORIDES

TECHNETIUM SPECIATION UNDER PYROCHEMICAL CONDITIONS IN CHLORIDE SALT MELTS

DISSOLVED IN FUSED SALT:	**SEDIMENT:**	**GAS-OFF:**	**ELECTRODEPOSITE**
Reduc.:$K_2Tc_2Cl_6$ $K_3Tc_2Cl_8$ Oxid.: TcO_3Cl, $TcOCl_4$	Tc metal Tc-Rh-Ru alloys TcO_2(?) Tc_4O_5(?)	Tc_2O_7 TcO_3Cl $TcCl_6$ $TcCl_5$	Tc METAL : Tc-Rh-Ru alloys TcO_2(?) REDUCED Tc CHLORIDES

Fig 1. Radiochemical hutch of ROBL/ESRF

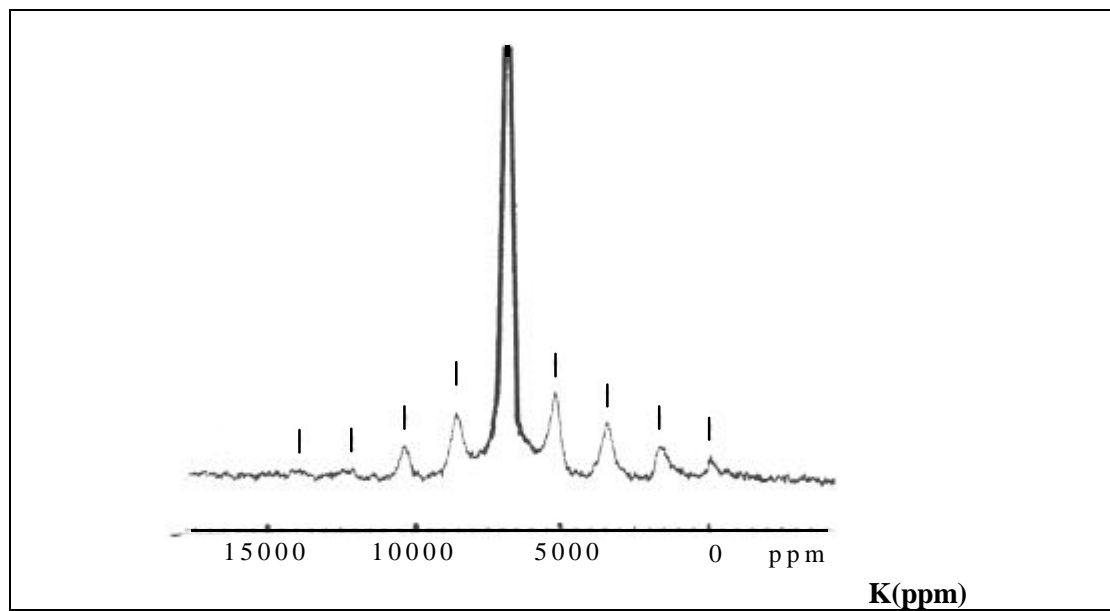Fig 2. NMR-^{99}Tc spectrum of Tc metal powder ($\hat{O}$ 80-150 ìm)
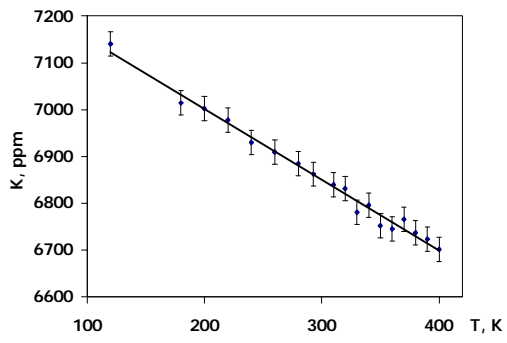
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Fig.3. Temperature dependence of isotropic
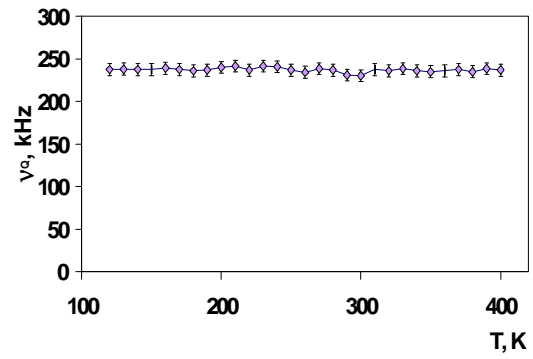Knight shift (K) for Tc metal powder

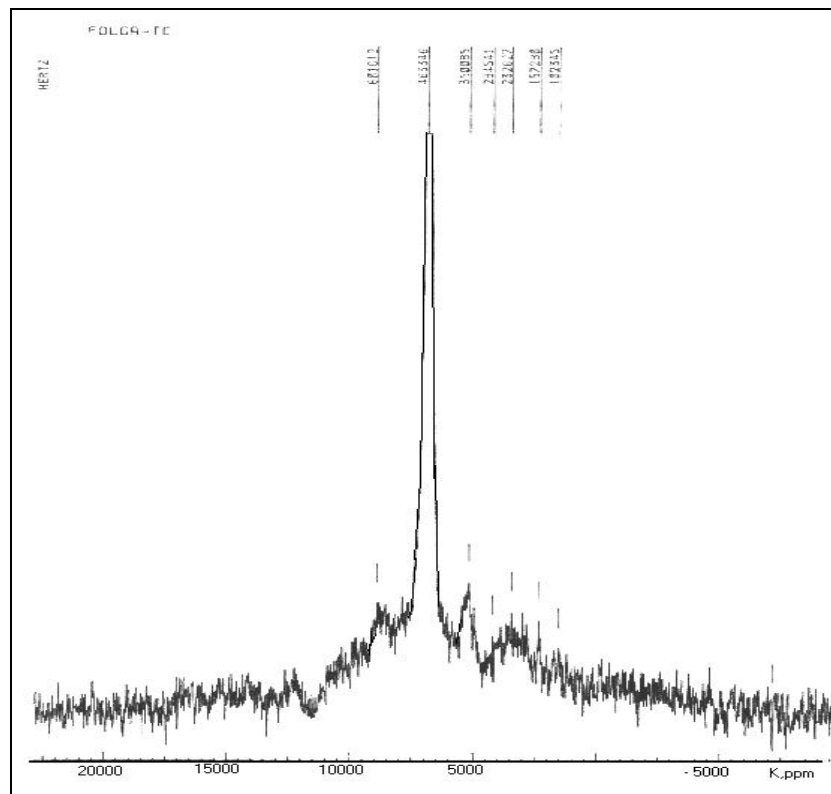Fig.4. Temperature dependence of ν_Q for
Tc metal powder

Fig.5. ^{99}Tc-NMR spectrum of Tc foil (d = 20 μm):
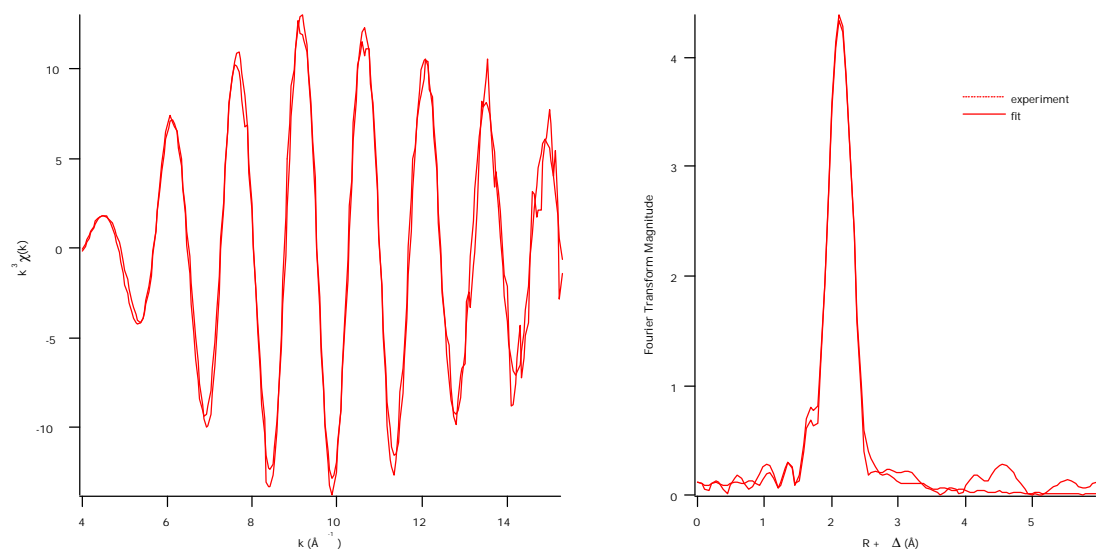
Fig. 6. Tc K-edge k^3-weighted EXAFS and corresponding Fourier transform of sample $(Me_4N)_2TcBr_6$: EXAFS structural parameters:

Tc-Br   N=5.8(2)   R=2.51(2) Å σ^2=0.0040 Å^2 $\Delta E0$=-16.9(5) eV

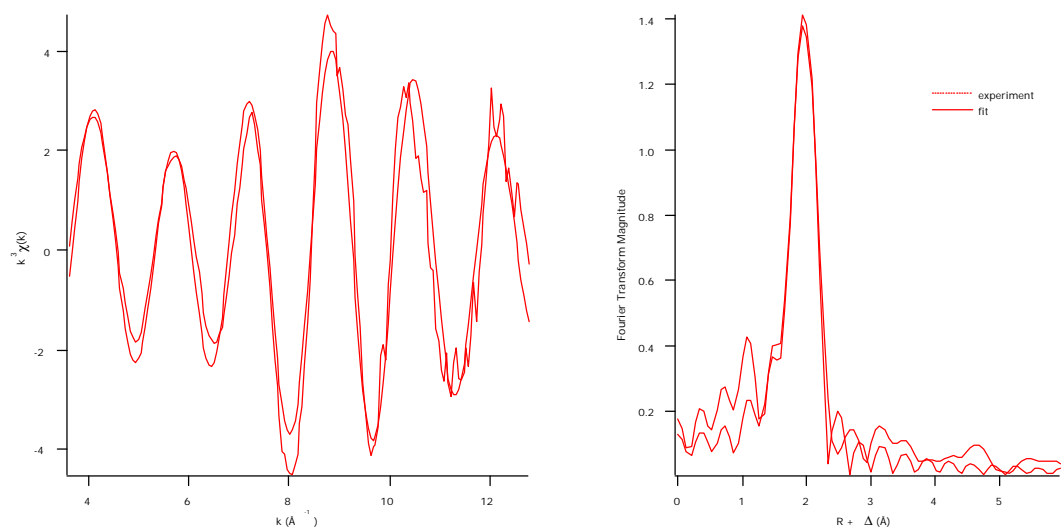**Fig. 7.** Tc K-edge k^3-weighted EXAFS and corresponding Fourier transform of sample $K_3Tc_2Cl_8$ EXAFS structural parameters for $K_3Tc_2Cl_8$ (preliminary approximation):

Tc-Tc   N=1.6(3)   R=2.20(2) Å σ^2=0.0069 Å^2 $\Delta E0$=-1.1(9) eV
Tc-Cl   N=2.2(4)   R=2.46(2) Å σ^2=0.0107 Å^2

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