ELECTRONIC STRUCTURE OF METALLIC TECHNETIUM CLUSTER MODELS USING DV-*Xa* CALCULATION

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Although several calculations of the metallic Tc electronic structure have been made since 80th years (see ref. in [1-2]), this problem has got new sound with the initiation of Tc transmutation projects and investigations of Tc-Ru alloys [3-4]. The results of the most of the calculations were not compared with the experimental data just because of the lack of such possibilities [1,5]. Practically all theoretical results were obtained by band theory of the solid state physics, enabling the authors to make some physic estimates. Meanwhile, less attention was paid to chemical aspects, better described by cluster models [2]. Our previous work [6] used such model, but it was limited by possibilities of X_a SW approach, especially its one or two sphere model limitations. In this work we present the results based on more accurate non-empirical X_a DV method using DVSCAT code [7]. We also increased both the dimensions and the variety of the clusters under study.

Recall that Tc metal exists in two modifications: the *hcp* for bulk metal and *fcc* for thin films and nanoparticles [8]. This requires taking into account two sets of models like in [6]. All model clusters were designed by consecutive extension of the spherical layers number around the allocated center. Both models with filled, and with the empty center were used for basic *hcp*-form. Some results are given below (Table 1 and Fig.1).

The use of program [7] provided us with an important advantage compared to [6] as it allowed the calculations using both symmetrized, and asymmetrized basis. The use of the symmetry essentially raised the speed of calculations but for applied Tc models it resulted in the incorrect description of electronic structure. In particular, the surplus of *5s*, *5p*- and deficiency of *4d*-electrons took place. Small peak appeared in occupied states spectrum (12eV for 36-hcp-sym in a Fig.1) in the area of more binding energies relatively the main *4d*-peak. This negative tendency amplified as the model size increased (Table 1). In opposite, the ignoring of symmetry gave the results, which were in good consistency with both band calculations (Fig.2) and experiment in the occupied spectrum (Fig.1) and for free states (Fig.3). The symmetry neglecting is not applicable to the subsequent study of the binary systems Tc-Ru which seem more plausible as asymmetrical cluster models.

Table 1. Metallic technetium cluster models *)

***LT*-N_a**	**R_c**	**N_c**	**R_n**	**R_{fc}**	***EC*(4d 5s 5p)**	***VB***	***VDN***	**N_f**
hcp-36	4.56	7.33	61.1	16.7	5.65 0.71 0.64	6.60	270	37.5
hcp-36 sym					5.20 0.76 1.03	9.93	308	53.8
hcp-39	4.74	7.08	59.0	2.6	5.65 0.72 0.63	6.53	272	38.8
hcp-57	5.47	8	66.7	22.8	5.66 0.69 0.65	6.75	254	36.8
hcp-57 sym					4.72 1.06 1.22	7.88	480	127.6
hcp-66	5.80	8	66.7	18.2	5.66 0.68 0.66	6.67	250	36.7
hcp-93 *sym*	6.80	8.26	68.8	22.6	4.61 1.04 1.35	8.60	475	121.5
fcc-19	3.68	6.32	52.6	5.3	5.64 0.73 0.63	6.10	275	53.4
fcc-43	4.51	7.26	60.5	2.3	5.70 0.68 0.62	6.87	248	72.1
fcc-55	5.20	7.85	65.5	23.6	5.72 0.66 0.62	6.76	232	67.1

*) Designation in the heading of the Table: N_a - number of atoms; R_c - radius of model, Å; *LT*-type of a lattice; N_c - average coordination number; R_n- relative coordination number in comparison with an ideal crystal, %; R_{fc}- a part of the completely coordinated atoms, %; *EC* - electronic configuration; *VB*- an estimation of valence band width, eV; *VDN* - average electron valence density at nucleus relative to $[TcO_4]^-$, %î; N_f - density of states at Fermi level, States / Ry Cell)

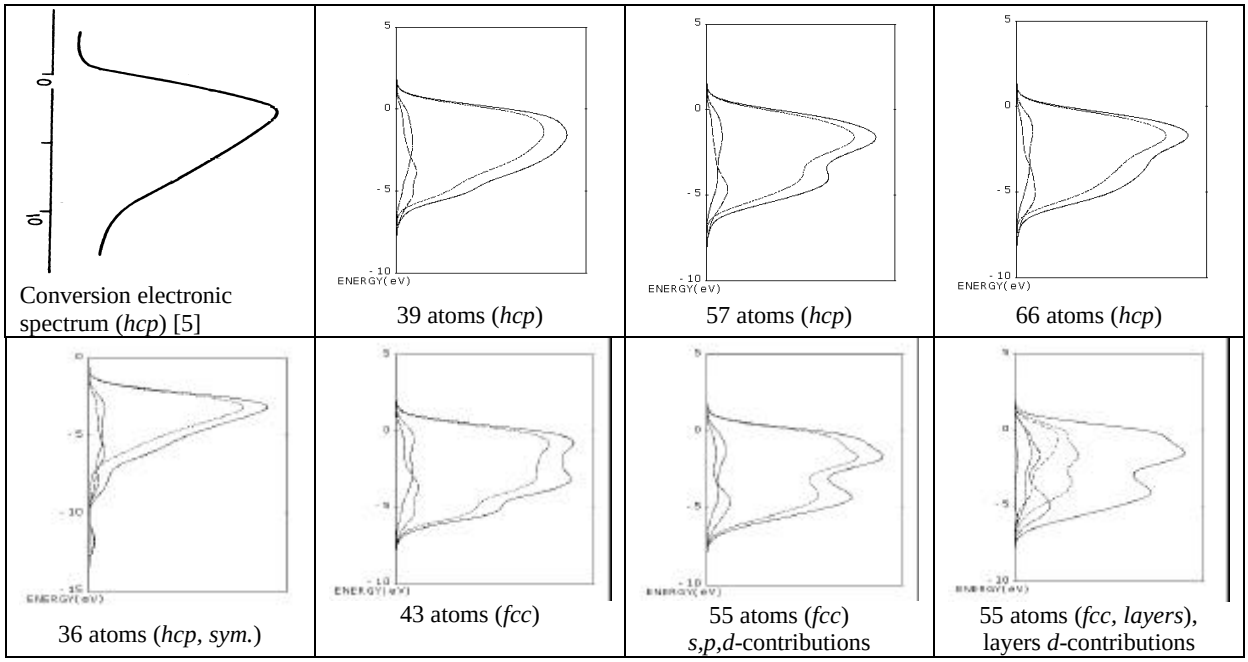
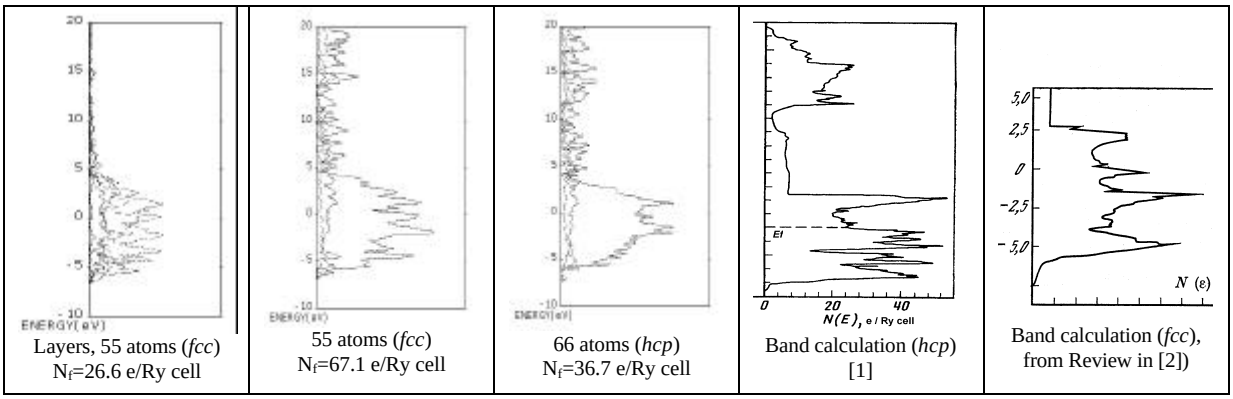


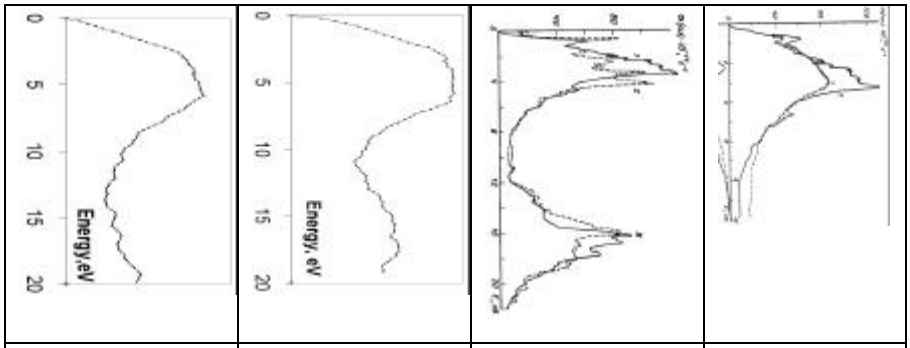
Fig.1 Partial (5s, 5p, 4d) and total electronic density of the occupied states.

Our calculations correspond to the results of band theory [1] about the similarity of electronic structure parameters for the both types of lattices. Similar distributions were got for all parts of spectrum. At the same time, there were also some divergences reflecting differences between some physical properties of these metal forms (for example, the temperatures of transition to superconducting state).



Layers, 55 atoms (*fcc*) N_f=26.6 e/Ry cell	55 atoms (*fcc*) N_f=67.1 e/Ry cell	66 atoms (*hcp*) N_f=36.7 e/Ry cell	Band calculation (*hcp*) [1]	Band calculation (*fcc*), from Review in [2])

Fig.2. Total Density of States



55 atoms (*fcc*)	66 atoms (*hcp*)	Band calculation (*hcp*) [1]	Experiment (0.62-10eV)[1]

Fig.3. Models of Interband Optical Conductivity

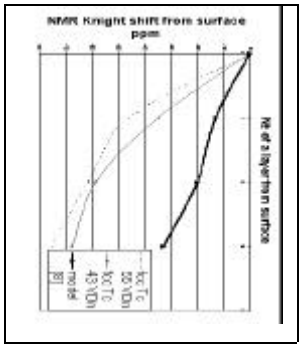


Fig.4. Layers Knight Shifts in Tc nanoparticles

Aiming to reproduce, more or less, the equivalence of atoms in a bulk crystal, we used the single average electronic density for all atoms. Contrary to this, for *fcc* Tc nanoparticle analyses, we took into account the non-equivalent layers (Fig.1, fcc-55 with layers). The features of electronic structure calculated with the layer model allowed to find correlation between Knight shifts in NMR spectrum [8] and electronic configuration of atoms in layers (Fig.4). Thus, the results confirmed the adequacy of both models (for bulk Tc metal and its nanoparticles, which could be used for the further study of Tc-Ru systems.

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