Atomic and electronic structure of free niobium nanoclusters: Simulation of the $M_{4,5}$-XANES spectrum of Nb$_{13}^+$

Antonina N. Kravtsova [a,*], Kirill A. Lomachenko [a,b], Alexander V. Soldatov [a,*],
Jennifer Meyer [c], Gereon Niedner-Schatteburg [c], Sergey Peredkov [d,1], Wolfgang
Eberhardt [e], Matthias Neeb [d,*]

[a] Research Center for Nanoscale Structure of Matter, Southern Federal University, Sorge str. 5, 344090 Rostov-on-Don, Russia
[b] Department of Chemistry and NIS Centre of Excellence, University of Turin, Via P. Giuria 7, 10125 Turin, Italy
[c] Technische Universität Kaiserslautern, Fachbereich Chemie und Forschungszentrum OPTIMAS, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Germany
[d] Helmholtz-Zentrum Berlin für Materialien und Energie, Wilhelm-Conrad-Röntgen-Campus Adlershof, Elektronenspeicherring BESSY II, Albert-Einstein-Straße 15, Berlin, Germany
[e] Technische Universität Berlin, IOAP, Straße des 17. Juni 135, 10623 Berlin, Germany

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ABSTRACT

The atomic and electronic structure of free niobium nanoclusters has been studied on the basis of X-ray absorption near-edge structure (XANES) spectroscopy and density functional theory. $M_{4,5}$-XANES spectra have been calculated for several structural models of the 13-atomic niobium cluster. The calculations have been done on the basis of both full multiple scattering theory within the muffin-tin approximation for a potential and full-potential finite difference method. The comparison of the experimental $M_{4,5}$-edge XANES spectrum (Peredkov et al., J. Electron Spectros. Relat. Phenomena 184 (2011) 113–118) with the simulated X-ray absorption spectra of Nb$_{13}^+$ hints to a highly-symmetric icosahedral structure of the cluster. An internuclear distance of 2.2 ± 0.1 Å between neighboring "surface" atoms of the icosahedron and 2.09 Å between the central "bulk" atom and "surface" atoms, respectively, has been found upon comparison of the experimental and theoretical XANES spectra.

1. Introduction

Nanoclusters attract significant attention both from the fundamental point of view and from the standpoint of their possible applications in nanotechnologies. The properties of nanoclusters change significantly with size and atomic structure [1,2]. Thus, a deep insight into the nature of nanoclusters is impossible without the data on their atomic structure. Such data can most reliably be obtained by studying free clusters, because deposition on any kind of substrate might cause major changes in clusters geometry and electronic structure.

Among the wide variety of different types of clusters, nanoclusters of 4d transition metals are of particular interest because of their fundamental importance and potential applications as magnetic materials and nanocatalysts. Niobium nanoclusters are among the most extensively investigated transition-metal clusters due to the several features, such as the relatively large propensity for clusterization and the existence of ferroelectric state related to superconductivity [3]. Atomic and electronic structure of niobium nanoclusters has been previously studied by various experimental and theoretical methods. Niobium trimers Nb$_3$ in argon matrices have been investigated based on an analysis of absorption (scattering depletion) and Raman spectra [4]. Photoelectron spectra of mass-separated Nb$_n^-$ clusters (n = 6-17) have been discussed by Kietzmann et al. [5], indicating a closed electronic shell of the neutral even-numbered clusters. Time-of-flight mass spectra of free niobium clusters Nb$_n$ produced by laser vaporization have been

measured and magic numbers were observed at $n = 7, 13, 15, 22$ [6]. Theoretical methods of investigation have been applied to determine the most stable atomic geometries and electronic properties of niobium nanoclusters in the size range from 2 till 52 atoms [7–14]. Atomic structure and magnetic moment of $4d$ transition-metal clusters with 13 atoms (including Nb_{13} cluster) have been discussed [15–18].

An effective modern technique for the analysis of nanoscale atomic structure (as well as the density of unoccupied electronic states near the bottom of the conduction band) is the X-ray Absorption Near-Edge Structure (XANES) spectroscopy [19,20]. XANES spectroscopy could give full information on the local atomic structure around the absorbing atom (coordination numbers, bond lengths and bond angles) with high precision, even for materials without long-range order in the atomic arrangement, such as nanoclusters. The bond length distances can be determined using XANES spectroscopy with the accuracy up to 0.02 Å, bond angles—with the accuracy of few degrees [21]. At the same time, the extraction of structural data from XANES spectra demands complicated theoretical analysis [22,23]. Recently, XANES spectroscopy has been successfully applied to investigate titanium and copper nanoclusters [24–26]. In the present work, the theoretical analysis of the $M_{4,5}$ XANES spectrum of free Nb_{13}^+ has been performed and compared with the recently measured experimental spectrum [27] in order to extract information on the geometry of the nanoclusters.

2. Experiment

The experimental setup used to measure $M_{4,5}$-XANES spectra of free mass-selected niobium clusters has been described in detail elsewhere [27,28]. In short, X-ray absorption spectra of free Nb_{13}^+ were measured at UE52-PGM beamline ($\sim 10^{12}$ photons/s, 1st undulator harmonics) of the synchrotron source BESSY II (Helmholtz-Zentrum Berlin, Germany). A cluster beam has been produced by pulsed laser vaporization (532 nm, 20 Hz) and supersonic expansion using a synchronized pulsed He buffer gas. Clusters have been mass-selected by using a Penning-like ion trap and FT-ICR mass spectrometer (7 T, Bruker). Fig. 1 shows the ICR-mass spectrum of mass-isolated Nb_{13}^+ clusters. Note the low degree of contamination after mass-selection and isolation. X-ray absorption spectra on Nb_{13}^+ have been recorded near the $M_{4,5}$-absorption edge of niobium using linearly polarized X-ray undulator radiation. As absorption signal, the number of ionic fragments has been recorded inside the ion trap (Fig. 2). The photon energy scans in Fig. 2 have been taken with the same mass-isolation parameters as were used to record Fig. 1. The two smallest fragment
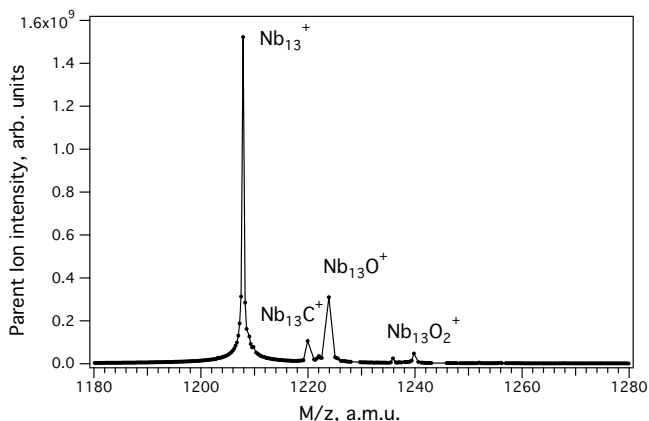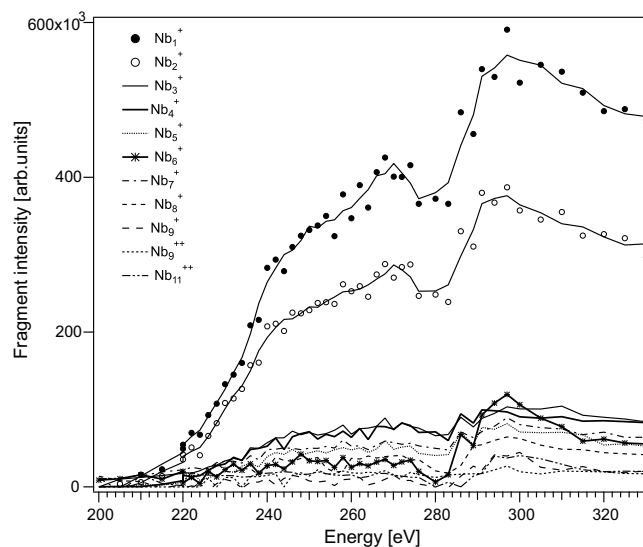

Fig. 2. Mass-resolved ion yield absorption spectra of Nb_{13}^+ recorded at the $M_{4,5}$-edge using soft X-ray undulator radiation (linear polarization).

ions (Nb_1^+, Nb_2^+) were the dominant ones and therefore they have been accumulated to represent the absorption spectrum of Nb_{13}^+ at best signal-to-noise ratio. The accumulated absorption spectra are shown as top curves in Figs. 4 and 6 (experimental spectrum). The fragmentation yield has been normalized to the photon flux of the beamline which was recorded by a GaAs-diode behind the monochromator exit slit. The second order light intensity (>500 eV) transmitted by the monochromator (plane grating) has been measured by us to be 2-3% of the first order intensity. Absorption by carbon and oxygen contaminated Nb_{13}^+-clusters can be ruled out by the tiny degree of contamination (Fig. 1) and the low degree of transmitted second order light. The ICR-cell has been quenched and refilled by new mother clusters after a few seconds of irradiation.

3. Computational details

Theoretical Nb $M_{4,5}$-XANES spectra for several structural models of 13-atomic niobium cluster have been calculated on the basis of two approaches.

First, the self-consistent real-space full multiple-scattering (FMS) theory has been used. The calculations are based on the formalism of the relativistic Green's function in the real space. The muffin-tin approximation [29] for the potential shape has been employed. This theory is implemented into the X-ray absorption spectra and electronic structure FEFF 8.4 code [30].

Secondly, the real-space full-potential finite difference method (FDM) realized in FDMNES2009 program code [31] has been applied. Its main advantage is the possibility to have a totally free potential shape, thus avoiding limitations associated with the classical muffin-tin approximation for a cluster potential.

Calculations of the Nb $M_{4,5}$-XANES spectra using both methods have been done within the Hedin–Lundquist model of the exchange-correlation potential taking into consideration a core hole effect.

Recently, FEFF code based on muffin-tin approximation has been applied to calculate the $M_{4,5}$-XANES spectrum of icosahedral Nb_{13} in which the surface atoms have been considered as absorbing atom [28]. In the present study we use not only FEFF, but also FDMNES code, to exhibit the influence of non-muffin-tin effects. Such effects are particularly important to be considered in the simulations of nanoclusters due to the significant "surface" atoms contribution

**Fig. 1.** ICR-mass spectrum of parent Nb_{13}^+ clusters after mass-isolation.

to the cluster's electronic structure. Moreover, Nb $M_{4,5}$-edge spectra have independently been simulated for both the "surface" and central ("bulk") atom of the icosahedron.

The atomic geometry of the structural models of Nb_{13}^+ has been optimized on the basis of the Kohn-Sham density functional theory using the ADF2009 program code [32] within the generalized gradient approximation (GGA) using the OLYP [33,34] model for the exchange-correlation potential. This model was chosen among other tested models (PBE, OPBE, BLYP), as it results in better agreement between theoretical and experimental values of the dimer bond length. The experimental value of the Nb_2-bond length is equal to $d_{Nb} \sim 2.08$ Å [35,36]. Our calculation of the dimer bond length performed within the OLYP exchange-correlation model results in a value of $d_{Nb} = 2.07$ Å, while the calculation done within the OPBE model results in $d_{Nb} = 2.03$ Å. For cluster geometry optimization a core double zeta, valence triple zeta, polarized basis set (TZP) [37] of Slater-type orbitals has been used. The positive charge of Nb_{13}^+ cluster has been taken into account.

The FDM scheme has previously been successfully applied to compute X-ray absorption near-edge spectra of metal nanoclusters, for example, small titanium [24] and copper [25,26] nanoclusters. The DFT approach as realized in ADF code, on the other hand, has been successfully used to study the atomic geometries and electronic properties of free copper [25,26] and titanium [38] nanoclusters.

4. Results and discussion

At the first step the Nb $M_{4,5}$-edge XANES spectrum of bulk niobium was calculated to check the adequacy of the used theoretical approaches. The bulk niobium crystallizes in *bcc* structure with the lattice parameter $a = 3.30$ Å [39]. A comparison of the theoretical Nb $M_{4,5}$-XANES spectrum of bulk niobium simulated on the basis of the full-potential finite difference method with the corresponding experimental EELS spectrum taken from Olszta et al. [40] is presented in Fig. 3. It can be seen that the calculated spectrum is in good agreement with the experimental one. Minor discrepancies between the experimental and theoretical spectra may be caused by the sample surface oxidation. An agreement between
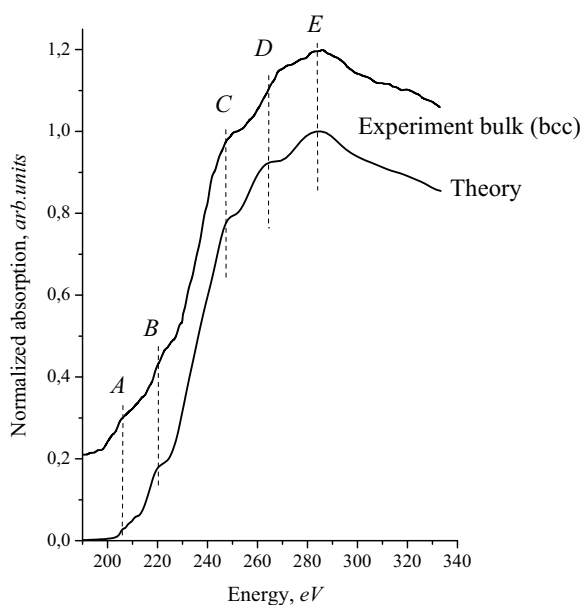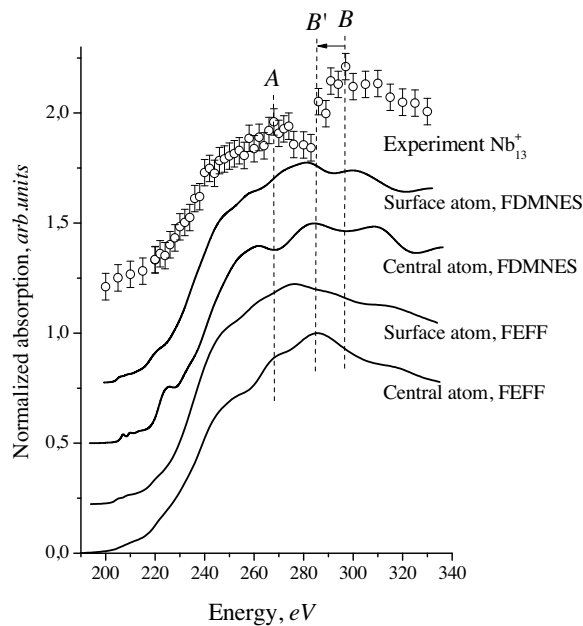
the theoretical and experimental spectra of bulk niobium supports the application of the finite difference method for the analysis of XANES of niobium nanoclusters.

Initially, the icosahedral model of the Nb_{13} cluster structure was considered. The lattice parameter $a = 3.30$ Å of a *bcc* niobium crystal gives rise to an interatomic bulk distance of $r = 2.86$Å $\left(r = a/2\sqrt{3}\right)$ which was used as initial guess of the distance between the "surface" atoms ($d_{surf-surf}$) of icosahedral Nb_{13}. The distance between the central atom and the "surface" atoms ($d_{cent-surf}$) of an icosahedron is generally related to $d_{cent-surf} = 1/2\sqrt{(1+\phi^2)}d_{surf-surf}$ where ϕ is the so-called Fibonacci number 1.618. Using the interatomic bulk distance as initial guess for the distance of the surface atoms of the icosahedron ($d_{surf-surf} = 2.86$ Å) the distance between the central and "surface" atoms is equal to 2.72 Å. Fig. 4 compares the experimental $M_{4,5}$-edge X-ray absorption spectrum of Nb_{13}^+ ($M_{4,5}$ edge) with the theoretical spectra calculated for the icosahedral structure of the 13-atomic cluster using the bulk atomic distance as initial guess for the "surface" atom distance. The displayed theoretical spectra are computed on the basis of both full-multiple scattering theory within the muffin-tin approximation for the potential shape (FEFF8.4 program) and full-potential finite difference method (FDMNES code). The spectra were simulated for the cases when both "surface" and central atoms were sequentially set as the absorbers. It can be seen from Fig. 4 that fine structures of the experimental and theoretical spectra contain features marked as *A* and *B*. However, maxima *B* of the theoretical spectra calculated on the basis of both FMS and FDM methods are shifted to the lower energy region as compared to maximum *B* of the experimental spectrum. The disagreement between the experimental and theoretical data (difference in the intensity of peak *A* and energy position of peak *B*) suggests for a refinement of the initially considered structural model of 13-atomic niobium cluster which is described in the following paragraph.

To further improve the agreement between theory and experiment the calculations of the Nb $M_{4,5}$-XANES spectra have been carried out for the icosahedral structural model of Nb_{13} varying the interatomic distances (calculations have been done for $d_{surf-surf}$ equal to 2.86 Å, 2.36 Å, 2.2 Å, 2.1 Å). A good agreement between

Fig. 3. Comparison of the $M_{4,5}$-XANES spectrum of bulk niobium (bcc structure) calculated on the basis of the full-potential finite difference method (FDMNES code) with the corresponding experimental EELS spectrum from Olszta et al. [40].
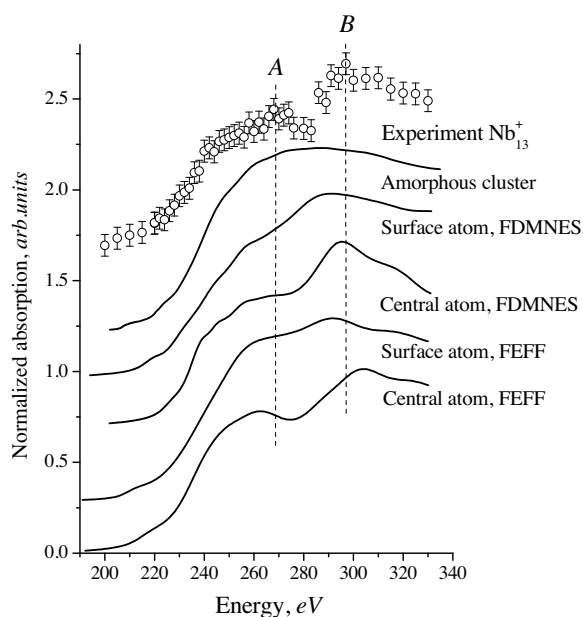

Fig. 4. Experimental $M_{4,5}$-XANES spectrum of free Nb_{13}^+ [27] compared to the theoretical spectra (FDMNES and FEFF) calculated for an icosahedral structure with an atomic distance between surface atoms equal to that of the crystalline bulk (2.86 Å).
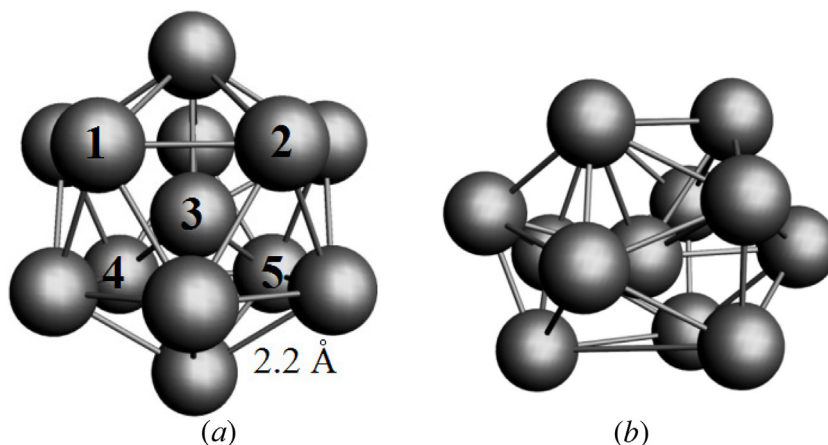
Fig. 5. (a) Schematic representation of the icosahedral structure of the Nb_{13} cluster used for calculation of the $M_{4,5}$-XANES spectra shown in Fig. 6. Labels 1-2-3-4-5 mark atoms laying in the plane used for calculations of a contour map of the potential of the niobium cluster (see Fig. 7). (b) Scheme of the "amorphous" structure obtained by atomic geometry optimization based on density functional theory implemented in the ADF code (see text).

experiment and theory is achieved when the internuclear distance between neighboring "surface" atoms is equal to $d_{surf-surf} = 2.2\,Å$. For this surface atom separation a distance from the center atom to the surface atoms of $d_{cent-surf} = 2.09\,Å$ results (Fig. 5a). This bond-length reduction agrees with the general tendency of decreasing interatomic distances with decreasing nanoparticles size [41]. We suppose that the significant bond length reduction in Nb_{13} as compared to bulk niobium is not only due to coordination change but also due to change in chemical bonding from metallic (in macroscopic particles) to covalent one (in small clusters). Note that the interatomic distance of molecular Nb_2 is $2.08\,Å$ [35,36], i.e. similar to the bond length between the central and surface atoms of the Nb_{13}^+-icosahedron which results in the best agreement of the theoretical with the experimental XANES spectrum as shown in Fig. 6.


Fig. 6. Experimental $M_{4,5}$-edge XANES spectrum of free Nb_{13}^+ [27] with the corresponding theoretical spectra (FDMNES, FEFF) calculated for the icosahedral structure having a distance between the "surface" atoms of $2.2\,Å$. Note that the simulated FDMNES spectrum of the amorphous structure shows definitely less fine structure than the spectra of the icosahedrons.

Fig. 6 shows theoretical XANES spectra simulated for the icosahedron of Nb_{13}^+ with distances $d_{surf-surf} = 2.2\,Å$ and $d_{cent-surf} = 2.09\,Å$. The simulations have been done on the basis of the full multiple scattering theory within the muffin-tin approximation for the potential shape (FEFF8.4 code) and the full-potential finite difference method (FDMNES code). For both types of calculations the "surface" and center "bulk" atom have been individually chosen as photon absorber. It can be seen that FDMNES calculations of XANES spectra are in slightly better agreement with the experiment as compared with FEFF8.4 calculations, what can be explained by the presence of non-muffin-tin effects due to the surface contribution to the electronic structure of the cluster.

Finally, the optimization of the atomic geometry of the Nb_{13}^+ cluster was additionally performed based on the DFT implemented in the ADF code [32]. As described above the icosahedral model was used as starting structure for the optimization. Without symmetry restrictions during the optimization, an "amorphous" cluster is obtained. In other words, all atoms of the cluster become nonequivalent (see Fig. 5b). Theoretical Nb $M_{4,5}$-XANES spectra of the amorphous cluster structure have been calculated based on the full-potential finite difference method (FDMNES code) for all nonequivalent niobium positions of the obtained structure (every nonequivalent niobium atom was sequentially set up as an absorbing one). To get a final theoretical $M_{4,5}$-edge inner-shell absorption curve, XANES spectra for all nonequivalent positions were summed up. The theoretical $M_{4,5}$-edge XANES spectrum for the "amorphous" structure of Nb_{13}^+ cluster is presented in Fig. 6. It can be seen that the calculated spectrum of the "amorphous" cluster shows much less fine structure than those of the icosahedron (experimental features marked as A and B are not reproduced in the theoretical spectrum of the "amorphous" structure). The inequivalent atoms of the amorphous structure gives rise to slightly different absorption spectra which superimpose to a featureless total spectrum. Thus the insufficient agreement between experiment and theory indicates that the "amorphous" structure is less likely. In other words, the measured spectral fine structure favours a high symmetry of the 13-atomic niobium cluster which is formed under the chosen experimental conditions. The performed analysis allows for the conclusion that the icosahedron with the distance between the "surface" atoms of ~2.2 Å is the most preferable structure of the 13-atomic niobium cluster among the considered models.

The FDMNES code was also used to calculate a contour map of the potential of the 13-atomic icosahedral niobium cluster within one of the icosahedral symmetry planes containing the central atom and four "surface" atoms (the plane containing atoms marked
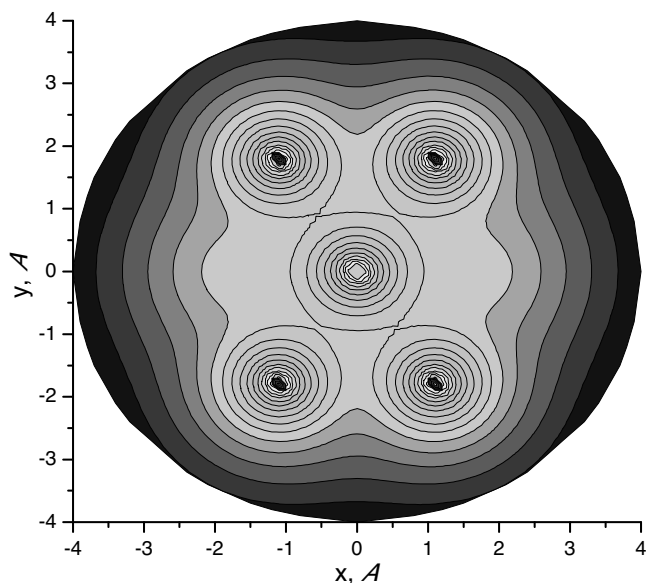
Fig. 7. Contour map of the potential of the 13-atomic icosahedral niobium cluster along the plane containing the central atom and four "surface" atoms. Darker areas correspond to weaker potential.

as 1-2-3-4-5 in Fig. 5a). The contour map of the potential of Nb_{13} is shown in Fig. 7. One can see that the muffin-tin approximation [29] is not valid for "surface" atoms of the Nb_{13} cluster. Within the muffin-tin approximation, the potential between atoms must be constant; thus, the potential along the line from the surface atoms to the outer region must be constant. From Fig. 7 it can be seen that this is not the case of Nb_{13} cluster, as the potential is changing significantly. Thus, full-potential methods like FDMNES seems to
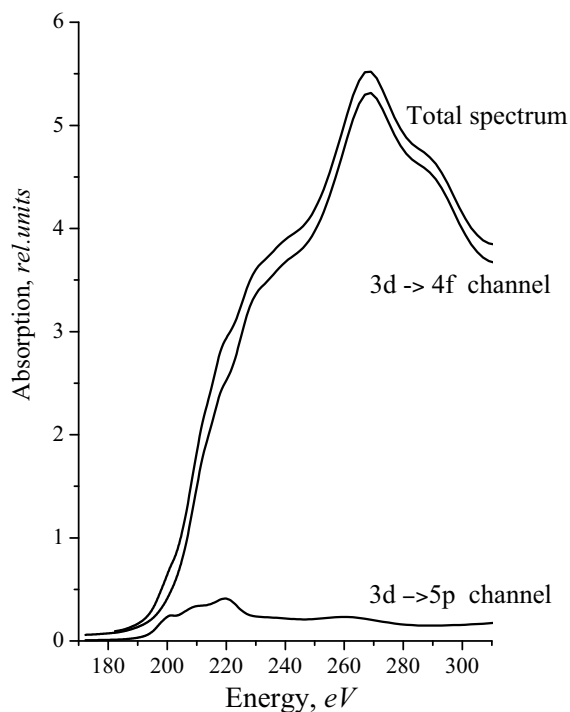
Fig. 8. Calculated $3d \rightarrow 4f$ and $3d \rightarrow 5p$ electronic transitions corresponding to the $M_{4,5}$-XANES of central niobium atom of icosahedral structure of 13-atomic niobium cluster (distance between the "surface" atoms is 2.2 Å). The total $M_{4,5}$-XANES spectrum calculated with the consideration of both Nb $3d \rightarrow 4f$ and Nb $3d \rightarrow 5p$ channels are also presented.

be most appropriate to simulate XANES spectra of small niobium nanoclusters.

According to dipole selection rules, the electronic transition corresponding to the Nb $M_{4,5}$-XANES includes two $\Delta l = \pm 1$ channels: $3d \rightarrow 4f$ and $3d \rightarrow 5p$. In the present work $M_{4,5}$-XANES spectra for all considered structural models of niobium clusters have been calculated as a sum of two dipole allowed channels. The possibility of different transitions of $3d$ electrons by photon absorption in niobium has been discussed earlier [42]. As an example, Fig. 8 shows the calculations of two channels ($d \rightarrow f$ and $d \rightarrow p$) corresponding to the $M_{4,5}$-XANES of central niobium of icosahedral structure of 13-atomic niobium cluster with 2.2 Å distance between the "surface" atoms. It can be seen that the $d \rightarrow f$ transition contributes much more than the $d \rightarrow p$ transition to the Nb $M_{4,5}$-XANES spectrum, which is similar to earlier results on bulk niobium [42].

5. Conclusions

Theoretical analysis of the $M_{4,5}$-edge X-ray absorption spectra of $Nb_{13}{}^{+}$ clusters has been performed and compared with experimental results. The Nb $M_{4,5}$-XANES spectra have been calculated on the basis of the full multiple scattering theory (FEFF8.4 code) and the full-potential finite difference method (FDMNES code) for several structural models of the cluster. XANES analysis has shown that high-symmetrical icosahedral structure of the 13-atomic niobium cluster is more preferable than the thermodynamically more stable "amorphous" one. The best agreement of the theoretical $M_{4,5}$-XANES with the experiment has been obtained for the icosahedral niobium clusters with the distances between the "surface" atoms of 2.2 ± 0.1 Å.

Acknowledgements

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