Calculations of chemical shifts of x-ray emission spectra and effective states of Nb atom in the Niobates

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A computational approach to evaluation of chemical shifts of characteristic X-ray emission lines of d and f element in different chemical compounds is proposed. It is based on modeling the embedded cluster electronic structure using relativistic pseudopotential approximation that is followed by restoration of (all-electron) wavefunction in the core region. The proposed approach is applied to the Nb K_α lines in fersmite. The line positions and their shifts with respect to those of metallic Nb were evaluated via the restoration of the all-electron wavefunction in the Nb core region. The results are in satisfactory agreement with the experiment, overestimating the measured value by $\sim 20\%$.

Introduction

According to modern concepts of closed nuclear fuel cycle, the immobilization and conservation of the actinide fraction is provided for in the form of chemically stable and radiation-resistant matrices, which is to be followed by their long-term storage in deep geological formations. As the most promising matrix materials, some synthetic mineral-like composites are regarded and some uranium and thorium containing accessor minerals can serve as the composites natural analogues, many of which have been in existence for hundreds of millions or even for billions of years. Hence, a study on these natural formations, of their stability to aggressive factors of the environment, of post-effects of nuclear-chemical- and radiation-induced chemical processes, of the physico-chemical state of the f- and d-elements in such minerals, could provide important prog-

nostic information on the immobilization properties of synthetic matrices to be used for high-level radioactive waste (HLW) disposal. In particular, the niobium-(titanium-tantalum) based complex oxides AB_2O_6 are considered to be some of perspective actinide-containing matrices; their natural analogues being minerals euxenite, aeschynite polycrase, and the general chemical formula, $(Ca,TR,U,Th)(Nb,Ta,Ti)_2O_6$, where TR stands for "terrae rarae" (lat.), or "rare earth" elements.

The metamict degradation, as an amorphization of the mineral structure, is an important consequence of the radioactive decay. Therefore, one of the important issues here is chemical consequences of the mineral matamictization, i.e. evolution of the physical-chemical states of atoms in the A- and B-groups and, in particular, red-ox states of the polyvalent atoms which are f- and d-elements here. While studying aeschynite and euxenite, Ewing *et al.* have found that amorphization of the mineral occurs in atomic displacement cascades initiated by alpha-recoil atoms and affecting several thousands of lattice atoms [1]. As the alpha-

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decay dose increases, individual cascades overlap, and gradually occupy the mineral volume. A chemical consequence of amorphization of euxenite and aeschynite [2] consists of breaking of the dioctahedric chains in $(Nb,Ta,Ti)_2O_{10}$ and a spatial distortion of the octahedrons formed by the Nb, Ta and Ti atoms with the oxygen ligands. At the same time, there are insignificant changes observed in the first coordination sphere of the B-position ($Nb-O_6$ etc.) atoms: a small decrease of the coordination number and of the bond lengths. When there is a transformation occuring of euxenite and aeshynite into the metamict state, the main damage is observed in the second coordination sphere, namely, it is the inclination angle of the cationic coordination polyhedron that is changed. The damage of the second coordination sphere that leads to the loss of the long-range order and of the crystal periodicity, was clearly observed in the EXAFS and XANES [3] spectra, but there was no significant difference found between the Nb-O bond lengths of the crystal and metamict samarskite ($AB_{1.7}O_{5.3}$). As to the stability of the AB_2X_6 group of minerals to post-effects of the radioactive decay, there is a positive influence observed of the high ionicity of the Nb-O bond. The papers cited here are only few among those devoted to studies of physical-chemical state of the group B atoms. However, these are related rather to structural or geometrical changes in the octahedral polyhedron system. There were no significant data obtained on the electronic subsystems of these atoms.

The aim of the present work is to provide some theoretical estimates for chemical shifts of the $K\alpha$-line of niobium, which enable, as we believe, some correct data on the chemical state of niobium in metamict and crystalline samples of the AB_2O_6 group of minerals, as well as thermochemical processes in various minerals of this type to be studied.

I.   Cluster modeling technique

Theoretical modeling of localized phenomena in solids comprising d- and f-elements by density functional theory (DFT) techniques for extended periodic systems encounters serious problems arising from the unavailability of advanced meta-gradient and, particularly, hybrid functionals and basis set restrictions. An attractive alternative consists in cutting a cluster which can be studied by non-periodical ("molecular") techniques (i.e. using so-called embedded cluster model [4]). Provided that the process (or property) of interest is localized at a single atom, one should reproduce some important characteristics of the surroundings of this atom to preserve the electronic structure around the atom with appropriate accuracy.

To determine an appropriate set of embedding data for the cluster modeling we have performed the calculations of periodic $CaNb_2O_6$ structure at experimental geometry [5] using the OpenMX package [6, 7] and applying there the LSDA-CA functional [8]. To minimize uncertainties of the Mulliken population analysis (utilized in OpenMX) we used the minimal basis set: one radial function per each occupied shell.

While there are different approaches to construct appropriate cluster model (see Ref. [9–11] and references), in this paper we follow a way based on fitting the cluster characteristics such as charges or force field distributions to those in the solid.
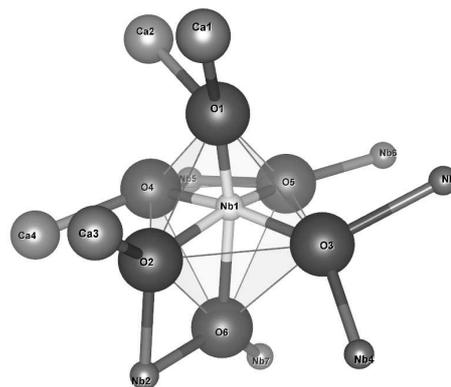

FIG. 1. The cluster model of the $CaNb_2O_6$. The central niobium atom Nb1 is surrounded by the six oxygen atoms O1–O6 in the first coordination sphere and niobium atoms Nb2–Nb7 and calcium atoms Ca1–Ca4 in the second coordination sphere. The first coordination sphere displayed as a crystal polyhedron.

In this scheme the central atom (Nb) and its first coordination sphere (6 oxygen atoms)

are included into the cluster as usually (being all-electron or conventional RECP-modeled elements). In turn, the atoms of second coordination sphere (Ca1–Ca4, Nb2–Nb7) are simulated by boundary "pseudo-atoms" (having a predefined reduced pseudo-charge and/or an operator describing the embedding) in order to make whole cluster neutral and with the closed shells only, while preserving most essential characteristics of the electronic distribution inside the cluster.

The boundary "pseudo-atoms" are currently described by some embedding potentials for corresponding atoms with reduced nuclear pseudo-charges. We assume here that the valence electrons of each boundary atom in the original solid crystal can be divided by some localization procedure into two parts: the first one that is located "inside" the cluster of interest, and the other one located "outside" the cluster. Next, we expect that effective core charge of a corresponding "pseudo-atom" should be equal to the number of electrons in first part, located inside the cluster. Thus, the cluster will be electrically neutral, while each border atom will have a charge, proportional to it's electronic contribution to a cluster area in the crystal.

To estimate electronic distribution of boundary atoms, we assume that the total valence electronic density of crystal can be divided into atomic (lone pairs, if exist) and diatomic parts (bonds), supposing that such bonds exist only between closest neighbours and that the valence electrons of each atom are distributed only among its bonds and lone pairs. If we find this distribution, we will know partial charges of the atoms.

In the case of simple crystals, like MgO [10] or ZrO_2 [9], this distribution can be trivially obtained from the symmetry of atomic surroundings. However, for more complex systems, like $CaNb_2O_6$ under study, which includes 5 non-equivalent atoms and 9 non-equivalent bonds, precise results cannot be easily determined, so that some estimations should be done.

We used several approaches to determine distribution of "atomic" electrons among bonds. In first one, we assume that each bond can be associated with one or more doubly occupied bond orbitals [9]. Requiring that total contribution of each atom to all its bonds is equal to its initial number of valence electrons, and sum of contributions to each bond from two involved atoms is twice the number of occupied orbitals, corresponding to this bond. We get a system of linear equations, which is undetermined, but we can choose a least-norm solution. The main drawback of this method is that it is "more mathematical than chemical", so that the results are fully determined by the number of valence electrons of each atom and bond topology.

In the second method we associate each bond with the part of valence electronic density between two atoms, which is is not obliged to be related to bond orbitals in any way. We calculate a "characteristic order" of each bond, in the present case, Mulliken overlap population and Mayer index, and assume that the valence electrons of each atom are distributed among its bonds proportionally to these orders. This method is much more "chemical" in its nature. However, unlike the previous one, it does not automatically provide integer number of electrons in the cluster, so, the results generally should be corrected.

Table I. Additional charges on atoms of the second coordination sphere of Nb in $CaNb_2O_6$ cluster model.

	I	II	III	IV
Ca1	1.08	0.42	0.50	0.35
Ca2	1.08	0.42	0.17	0.30
Ca3	1.08	0.17	0.33	0.35
Nb2	0.45	1.59	1.31	1.22
Ca4	1.08	0.17	0.33	0.30
Nb3	0.45	0.67	0.71	0.60
Nb4	0.45	0.67	0.33	0.35
Nb5	0.45	1.59	1.32	1.30
Nb6	0.45	0.67	0.99	0.91
Nb7	0.45	0.67	0.99	0.91

Additional charges obtained by (I) fitting the Nb1 Bader charge to that from periodic structure calculations (Bader atomic charges are given in the Table II); (II) associating the bonds with double-occupied orbitals; (III) distributing valence electrons according to Mulliken overlap population; (IV) distributing valence electrons according to Mayer index.

Additional positive charges located at the atoms of the second coordination sphere are

listed in Table I. We also provide the cluster model with the additional charges chosen to fit central Nb atom Bader [12, 13] charge to that from periodic structure calculations.

II. Computations of the X-ray emission spectra chemical shifts of Niobium in CaNb$_2$O$_6$

Chemical shifts of Niobium K$_\alpha$ lines in solid CaNb$_2$O$_6$ with respect to metallic Nb are calculated using the cluster model described above. We employed the method described in our previous papers [14–16]. This method is based on the relativistic pseudopotential model and one-center restoration procedure [17, 18] to recover a proper all-electron structure in heavy-atom cores after the pseudopotential simulation of chemical compounds. In [14] the effective one-electron operator is constructed to obtain the chemical shifts values as difference between its mean values for considered compounds. In [15, 16] further improvement and generalization of this method are provided.

The results of these calculations are compared to the experimental datum on the niobium X-ray emission spectra (XES) chemical shift in the wiikite mineral with respect to the metallic niobium and chemical shifts computed as differences between corresponding transition energies obtained from the all-electron calculations of the periodic structures CaNb$_2$O$_6$ and metallic niobium.

Electronic structure calculations of the embedded cluster are performed in the framework of two-component DFT and relativistic pseudopotential model [19–21] using the code described in Ref. [22].

The exchange-correlation functional PBE0 [23] was used. For central niobium atom we employed the pseudopotential leaving 13 electrons for explicit treatment, while the atoms of the second coordination sphere were modeled with zero electron pseudopotentials.

In the equilibrium state of the system, the forces acting on each atom of the system compensate each other. We can express this condition in the following way. Let us denote the

coordinates of the central atom and the atoms in the first coordination sphere as $\{\vec{R}_i\}_{i=1}^N$, the additional charges of atoms of 2nd coordination sphere as $\{Q_j\}_{j=1}^M$ and consider the total energy of the system U as function of $\{\vec{R}_i\}$ and $\{Q_j\}$.

Then we define the quantity

$$\Phi = \sum |\vec{\Phi}_i|^2 = \sum \left| \frac{\partial U}{\partial \vec{R}_i} \right|^2 \qquad (1)$$

depending on the additional charges values and measuring the deviation of the force field in the cluster from that in the solid.

Table II. Bader atomic charges of central Nb atom and its 1st coordination sphere and deviations of the force field from that in solid.

	I[a]	II	III	IV	cryst.[b]
Nb	2.60	2.74	2.73	2.73	2.59
O	-1.38	-1.19	-1.17	-1.18	-1.06
O	-1.46	-1.29	-1.28	-1.28	-1.16
O	-1.38	-1.40	-1.36	-1.33	-1.16
O	-1.34	-1.06	-1.99	-1.01	-1.16
O	-1.33	-1.40	-1.51	-1.45	-1.16
O	-1.28	-1.09	-1.14	-1.08	-1.16
Φ^c	0.040	0.021	0.026	0.029	

[a]I, II, III and IV: see the legend in Table I.
[b]Data from CaNb$_2$O$_6$ periodic structure calculations.
[c]Total values of the squared force functional acting on the central atom and its first coordination sphere (defined in (1)).

Another criterion of the quality of the chosen cluster model is provided by the Bader charge analysis. The results of the Bader charge analysis and Φ values for all discussed cluster models are presented in Table II.

It follows from data listed in Table II that these two criteria can hardly be satisfied simultaneously.

The chemical shifts values for niobium in CaNb$_2$O$_6$ with respect to the metallic Nb are presented in Table III. Metallic Nb was modelled in two ways: as Nb$_2$ molecule and the single atom. The difference between chemical shifts values for these two references is about 10 meV by the order of magnitude. The different additional charges distributions give the results which differ from each other up to 100 meV. This demonstrates the importance of proper choice of

Table III. XES chemical shifts of the Nb K_α lines in the $CaNb_2O_6$ with respect to the neutral atom and Nb_2, meV.

	$2p_{1/2} \to 1s_{1/2}$	$2p_{3/2} \to 1s_{1/2}$
$CaNb_2O_6$, I[a] – Nb_2	-331	-349
$CaNb_2O_6$, II – Nb_2	-393	-412
$CaNb_2O_6$, III – Nb	-375	-406
$CaNb_2O_6$, III – Nb_2	-397	-416
$CaNb_2O_6$, IV – Nb_2	-391	-410
$CaNb_2O_6$[b] – Nb (met.)	-220	-215
expt.[c]	-264 ± 7	

[a]I, II, III and IV: see the legend in Table I.

[b]Result of all-electron calculations of the $CaNb_2O_6$ periodic structure and metallic niobium performed by WIEN2K code [24].

[c]Experimental datum on niobium chemical shifts in wiikite mineral with respect to metallic Nb, provided by one of the authors of the paper (E. F.) obtained by the method described in Ref. [25]. Although Fersmite and Wiikite are two different minerals, they share common NbO_6 structure modelled in our study, so one can expect the qualitative agreement between computational and experimental results.

distribution of additional charges. The experimental value 264 meV, is in qualitative agreement with the results obtained for the first model and the results obtained from all-electron DFT linearized augmented plane wave calculations of the periodic $CaNb_2O_6$ structure and metallic Niobium with using WIEN2K code. These calculations give results close to the experimental datum, although their quality cannot be considered as high, so, the close agreement can be rather interpreted as fortunate.

Conclusions

A computational approach to evaluation of chemical shifts of characteristic X-ray emission lines of d and f element in different chemical compounds is proposed. It is based on modeling the embedded cluster electronic structure using relativistic pseudopotential approximation that is followed by restoration of (all-electron) wavefunction in the core region. The proposed approach is applied to the Nb K_α lines in fersmite. The embedded cluster comprises the central atom (Nb) and those of its first coordination sphere as well as a set of pseudoatoms simulating the second coordination sphere. The pseudoatoms are simulated in such a way that the electrical neutrality of the cluster is maintained and the distribution of their electrons among chemical bonds is reflected. To determine the pseudoatoms uniquely, additional requirements were imposed (minimizing the force field in the inner part of the cluster or reproducing the infinite-crystal atomic charges for the central atom an its first coordination sphere). The emission line positions and their shifts with respect to those of metallic Nb were evaluated via the restoration of the all-electron wavefunction in the Nb core region. The results are in satisfactory agreement with the experiment, overestimating the measured value by $\sim 20\,\%$.

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