ELSEVIER

Journal of Alloys and Compounds 300–301 (2000) 348–352

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Mixed valency of the rare earth and actinium ions in solid states

N.A. Kulagin*

Institute for Chemistry, Kharkov State University, av. Shakespeare 6-48, 310045 Kharkov, Ukraine

---

Abstract

This paper is devoted to the theoretic and experimental study of thee electronic states of *n*f-ions in solids. The experimental and theoretical results show that the energy of X-ray lines decreases when the ion valency increases. The calculated N- and Z-dependences of energy X-ray lines and separate electrostatic parameters improve the reliability for prediction of spectra and mixed electronic states of rare earths and actinides in solid state, plasma and galaxy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rare earth; Actinide; Valency; X-ray line

---

1. Introduction

The ions with nf^N-configuration, i.e. ions of lanthan-4f and actinide-5f groups elements have been and continue to be, a thoroughly explored set of electronic systems. Wide employment of *n*f ions has stimulated investigations of the properties of solids with regular and impurity *n*f ions. The problem of mixed valency of these ions in solids has arisen in recent years. The determination of the concentration of the ions with various electronic states (valency) is one of the main problems of solid state physics.

The theoretical study of nf^N ions is, in general, realized in Hartree–Fock approximation with different modifications [1,2]. Calculated results for spectra of free and doped rare-earths (REs) and actinides (ACs) are good for quantitative and qualitative analysis [3,4]. Experimental and theoretical data have been obtained and published for REs and ACs (in short – RA) in various books and papers [1–16], in particular, in our books [5,6].

The analytical Z- and N-dependence for different parameters of ions has been used succesfully for the prediction of spectroscopic properties of some free and impurity ions [5–8]. Theoretical N-dependence of electrostatic parameters for nf^N-configurations are calculated in our paper [8] where Racah's technique is used. In reference [9] analytical dependencies for the energy of X-ray lines and energy of optical transition were obtained for 3d and 4f ions. In the first approximation the N-dependence of electrostatic parameters for nf^N configuration is linear at third-law dependence of energy levels [5,8].

The characteristic irradiation of regular 4f ions in solid states has been studied in detail for some compounds by Sumbaev et al. [11]. The experimental dependence of energy of K-X-ray lines of RE^{+n} ions with the number of 4f electrons is linear. The energy of K lines increases with the increase in the number of 4f electrons (decreases with the valency of RE ion).

Our book [5] and paper [9] contain the theoretical values for the energy of K and L lines for RE and in Ref. [10] we published similar data for AC ions. We used Hartree–Fock–Pauli approximation for free ions and for clusters and the relative error of some theoretical calculations is $<0.5\%$.

For ACs, experimental results are very scanty [12–16]. Spectra of impurity actinides are investigated by Carnall et al. [12]. Spectra of free actinides $5f^N$ 7s configurations are studied in [13–15]. Some experimental results for the energy of the X-ray lines of ACs are given in [16] which we use as a reference point for the estimation of the accuracy of the theoretical approach.

In this paper we study the electronic structure, energy of X-ray lines and valency of the ions with an unfilled *n*f shell. We have to consider the different valency of *n*f ions and we have to calculate the energy of X-ray lines, and, also the N- and Z-dependences of energy of X-ray lines and determine the mixed valency of separate ions in solids.

---

*Corresponding author.

E-mail address: kulagin@spin.univer.kharkov.ua (N.A. Kulagin)

0925-8388/00/$ – see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(99)00764-1

2. Theoretical procedure

For the calculation of the electronic structure of *n*f ions we used Hartree–Fock–Pauli (HFP) approach. For this method non-relativistic Hamiltonian can be written in standard form (in atomic units, a.e.):

$$\boldsymbol{H} = -1/2\sum_{i=1}^{N}\Delta_{\mathrm{i}} - \sum_{i=1}^{N} Z/r_{\mathrm{i}} + \sum_{i>j}^{N} 1/r_{\mathrm{ij}} \tag{1}$$

Minimization of the Hamiltonian (1) matrix elements, calculated on the basis of wave functions for nl^{N} configuration in the central field approximation, yields energy levels of the standard form [1–6]. Radial Slater's integral — F^{k}(nl,nl) in HFP—approximation is determined in [5,17]. The HFP method operates only with the main part of Breit's relativistic Hamiltonian: *v*-dependence of mass of electron, contact *C*(nl), and spin-contact Q(nl), interactions which were concluded in radial integrals and energy of the ion [5,6].

We have to calculate the electronic structure of nf^{N} configurations in the free state and RA^{+n}:$[\mathrm{L}]_k$ clusters by used of programmes described in [5]. Separate data of the calculations for *n*f ions were published in Refs. [6,10]. The results of calculations for one- and two-electrons parameters for RE and AC ions are in good agreement with data seen in the literature [1–4]. A lot of problems arise when we have to calculate the electronic structure of the configurations with the core's hole.

We consider the electronic structure of nf^{N} and $n'l'^{-1}nf^{\mathrm{N}}$ configurations and calculate the energy of the separate K and L X-ray lines of all RE and AC ions. We determine energy of X-ray lines as difference of average energy of $n''l''^{-1}nf^{\mathrm{N}}$ and $n'l'^{-1}nf^{\mathrm{N}}$ configurations with the full self-consistent field calculations for each configuration.

Separate results of calculations of energy of K- and L-X-ray lines for *n*f ions are presented in Table 1. It should be noted that energy of X-ray lines of all *n*f ions increases with the number of *n*f electrons. This is so-called a negative shift of X-ray lines when energy of X-ray lines diminishes when valency of ions increases. For RE ions we calculate the values of the shift of X-ray lines which are greater than for the ACs at 10–20%.

Comparing our results with the experimental data [16] we conclude that for K_α and K_β lines of *n*f ions deviation are typically 1–3%. For L lines of AC ions, for example, the situation is the following: for L_α lines the agreement is surprisingly good (deviation is near 0.5%) but for the next series it is much worse and reaches 6%.

Now we consider the change of energy of the X-ray lines with the valency of ions (so-called valency shift of X-ray lines). We determine the valency shift energy of X-ray lines (VSXL) as [9]

$$\Delta E_{\mathrm{x}} = E_{\mathrm{x}}^{+n} - E_{\mathrm{x}}^{+n+1} \tag{2}$$

where E_{x}^{+n} is energy of the X-ray line for an ion with $+n$ valency. The value of the energy of the X-ray line increases with the nucleus charge and the number of *n*f electrons.

For example, the value of VSXL according to Eq. (2) and the data of Table 1 for the AC^{+2} to AC^{+3} transition is of the order of 100 meV (see Table 1). For the K line of AC ions we obtain the highest value of VSXL and smallest the for L line. The change of energy of the K and other lines of RA ions with ionization of *n*f electron depends on the relative shifts of $n'l'$ and $n''l''$ shells.

The electronic density of external $(n+1)$s and $(n+1)$p electrons of RA ions participated into X-ray transition is described by the function with the nodal points and maximums in inner region of atom. And ionization of *n*f electron in order to significant interaction of electrons of *n*f and $(n+1)$s or $(n+1)$p shells set in motion of the n's and n'p electronic densities towards the inner region of ion. According to shift of these shells the value of screening constant changes for $n'l'$ and $n''l''$ electrons which are participating in X-ray transition. The value of the screening constant for the 1s shell-σ_{is}(for example, for K line) changes more than $\sigma_{2\mathrm{p}}$. As a result of our consideration the energy of $\mathrm{K}_{\alpha1}$ line decreases when the valency of *n*f ion increases.

Analysis of Table 1 permits the conclusion that there is

Table 1
Theoretical values of energy of K_α- and L_α-lines for RE and AC ions (in eV)

RE	E ($\mathrm{K}_{\alpha1}$)	E ($\mathrm{K}_{\beta1}$)	E ($\mathrm{L}_{\alpha1}$)	AC	E ($\mathrm{K}_{\alpha1}$)	E ($\mathrm{K}_{\beta1}$)	E ($\mathrm{L}_{\alpha1}$)
Nd^{+2}	37 337.290	42 250.942	5370.985	U^{+2}	95 912.345	108 809.007	13 639.793
Nd^{+3}	37 336.610	42 248.875	5369.708	U^{+3}	95 912.037	108 808.394	13 639.528
Nd^{+4}	37 335.741	42 246.471	5368.449	U^{+4}	95 911.663	108 807.659	13 639.200
Eu^{+2}	40 071.174	45 371.500	5852.357	Np^{+2}	98 307.960	111 517.588	13 970.953
Eu^{+3}	40 070.420	45 369.567	5848.793	Np^{+3}	98 307.642	111 516.963	13 970.674
Eu^{+4}	40 069.405	45 367.192	5847.622	Np^{+4}	98 307.262	111 516.221	13 970.346
Gd^{+2}	42 921.661	48 620.131	6062.622	Bk^{+2}	108 277.894	122 779.219	15 339.303
Gd^{+3}	42 920.521	48 618.235	6063.971	Bk^{+3}	108 277.543	122 778.545	15 339.005
Gd^{+4}	42 920.118	48 615.998	6060.614	Bk^{+4}	108 277.142	122 777.775	15 338.668
Yb^{+2}	52 156.939	58 580.850	7421.563				
Yb^{+3}	52 155.897	58 578.564	7426.668				
Yb^{+4}	52 155.007	58 576.031	7429.100				

a significant influence of ionization of *n*f electron on the disrtibution of the electronic density of the 1s shell. The change of the electronic state of 2p (3p) and 3d shells is slower and $E(\mathrm{K}_\alpha) > E(\mathrm{L}_\alpha)$.

The values of VSXL for K or L X-ray lines of RA ions were calculated with high accuracy. Using the modern experimental equipment (X-ray microanalisor or two-crystal X-ray spectrometer [18,19]) we can determine a relative concentration of the ions of different valency with an error of 7–10%. Analysis of the value of VSXL for $\mathrm{RA}^{+n}-\mathrm{RA}^{+n+1}$ transition is very interesting for a detailed investigation of actinides.

3. N- and Z-dependence of E_x and ΔE_x

Theoretical N-dependence of the electrostatic $F_k(nf,nf)$ and $\eta(nl)$ parameters and angular coefficients for energy levels of nf^N configurations of RE were studied in detail in Ref. [8]. Linear N-dependence of $F_k(nf,nf)$ are right for RA at first approximation only. Significant deviation of the N-dependence from linear for $F_k(nf,nf)$ and $\eta(nf)$ integrals we obtained for RA^{+n}- to $-\mathrm{RA}^{+n+1}$ transition. This well-known deviation realises for the first terms of RE and AC rows.

The theoretical foundation for the investigation of the N- and Z-dependence of energy of X-ray lines and electrostatic parameters $F_k(nl,n'l')$, $\eta(nl)$ for nl^N configurations was considered in Ref. [9]. As shown in this paper the N-dependence of the energy of X-ray lines in the first approximation is square-law dependence (see Table 2)

$$E_x = E_o + aN + bN^2 \tag{3}$$

For X-ray transition with significant interaction of nl' electrons with *n*f active shell (these are 4p or 4d electrons for lanthanides and 5p, 5d for actinides) we must operate to the full angular interaction of *n*l electrons with electrons participated into X-ray transition. And the final form of N-dependence is third-degree law to N [9]. For K and L lines of RE and AC we can use the Exp. (3) with a relatively high accuracy. The values of E_0, *a* and *b* parameters for RE were ploted in [9] and for AC ions are presented in Table 2. Results of the calculation of the value of the coefficients in Exp. (3) for K and L X-ray lines can be obtained easily. First of all, constant *a* is possitive and constant *b* is negative and smaller than the value of *a* for all X-ray lines (the ratio $|b|/a$ is 0.12–0.15 for Ac and 0.03–0.02 for No).

The Z-dependence of the *a* and *b* constants is linear: *a* increases according to Z from 0.431 for Ac to 1.035 for No and the values of $|b|$ decrease from 0.070 to 0.020. But the value of $|b|$ constant, for example, under Ac-to-Th transition changes from 0.070 to 0.034, i.e. we obtain the significant decrease of the $|b|$ values for $\mathrm{K}_{\alpha1}$ line. The change of the $|b|$ values for Ac $\mathrm{K}_{\beta1}$ line is as follows: 0.128 for Ac I and 0.071 for Ac IV. For the $\mathrm{L}_{\alpha1}$ line we observe essential increases of the $|b|$ parameter during the Ac–Th transition (0.003–0.036).

The Z-dependence of the E_o values for all X-ray lines can be described by square-law curve with high accuracy; the final form all data of Table 2 can be described by the formula

$$E_x = E_0(c + \alpha Z + \beta Z^2) + a(c' + \alpha' Z)N + b(c'' + \alpha'' Z)N^2 \tag{4}$$

where the values *Z*, *N* and constants are determined by the electronic state of the *n*f ion.

4. Experimental technique and results for regular and doped ions

We studed the electronic states and mixed valency of RE and separate AC ions in some crystals before and after

Table 2
N-dependence of X-ray lines of actinides (in eV)

Ion	$\mathrm{K}_{\alpha1}$ line			$\mathrm{K}_{\beta1}$ line			$\mathrm{L}_{\alpha1}$ line		
	E_o	a	$-b$	E_o	a	$-b$	E_o	a	$-b$
Ac	88 951.080	0.431	0.070	100 932.001	0.969	0.128	12 671.789	0.424	0.052
Th	91 233.519	0.467	0.034	106 137.129	0.938	0.071	12 989.542	0.326	0.032
Pa	93 553.072	0.540	0.034	106 137.129	1.052	0.064	13 311.565	0.479	0.030
U	95 910.145	0.605	0.033	108 801.672	1.162	0.061	13 637.868	0.535	0.029
Np	98 305.122	0.659	0.032	111 512.147	1.268	0.059	13 968.481	0.580	0.028
Pu	100 738.542	0.691	0.031	114 262.623	1.280	0.056	14 303.356	0.640	0.027
Am	103 210.648	0.724	0.030	117 047.368	1.430	0.052	14 641.226	0.682	0.026
Cf	105 721.613	0.767	0.028	119 881.368	1.487	0.049	14 986.249	0.711	0.025
Bk	108 272.134	0.826	0.026	122 758.559	1.586	0.047	15 334.323	0.728	0.023
Cf	110 862.572	0.882	0.025	128 645.240	1.631	0.045	15 686.806	0.740	0.021
Es	113 493.397	0.920	0.024	128 645.240	1.714	0.044	16 043.560	0.784	0.021
Fm	116 165.234	0.935	0.023	131 668.028	1.942	0.046	16 405.048	0.790	0.020
Md	118 877.847	0.977	0.022	134 708.967	1.906	0.044	16 770.396	0.851	0.020
No	124 428.762	1.035	0.021	140 974.978	2.221	0.042	17 140.694	0.875	0.019

γ-irradiation or thermal treatment. We used the modified microanalyser Cameca with dispersitional X-ray spectrometer. The experimental procedure was described in detail in Refs. [18–20].

First of all, we studied the chemical shift of the L lines for RE ions (Eu, Tm, Yb etc.) in fluoride compounds (REF_2–REF_3) and compared these data with energy for K_α lines which were received using the X-ray spectrometer of Sumbaev et al. [11].

We used an X-ray microanalysor, and the intensity of X-ray lines was determined for etalon and the examined crystals consistently (for crystal before and after treatment, for example) for each step of the crystal-analysor at one value of the crystalliser turn angle. Curves of intensity of X-ray lines were approximated by the lorentzian functions. The results which were obtained for different points of one sample differed by 1–3%. The accurancy of the determination of energy of the REL_α lines are ±180 meV while the accuracy for the MeK_α line is ±130 meV. For effective excitation of X-ray irradiation we used an electronic probe with energy at 2–3 times more than energy of the X-ray line. This is energy in the range 10–25 KeV. Electron penetration for that energy is 3–5 mkm, and we can alter the depth of the electron penetration with a change of the electrons' energy.

We studied the valency shift and the electronic state of separate RE ions in different compounds. First of all, Yb in: simple oxide (Yb_2O_3), perovskites (ABO_3), garnets ($Y_3Al_5O_{12}$) and some glasses; Tm ions in: TmS, Tm_2O_3 and TmF_x. Energy of X-ray lines and electronic states of the following doped ions: Nd, Eu Gd, Tb etc. ions were studied carefully. We also studied the electronic state of U ions in separate compounds.

Concentration of doped ions are $5\cdot10^{-2}$–10 wt%. γ-Irradiation (^{60}Co, 10–10^4 Gr) or thermal treatment of the samples in general leads to change of impurity's or the regular ions valency. Separate mechanisms of change of ions electronic states under treatment and γ-irradiation are described in our book [5]. After irradiation of crystals with different doped ions we have to study as increase or decrease of the valency of ions. For example, γ-irradiation of $YAlO_3$:Cr:Nd, garnets led to a shift of the CrK_α line at (0.36±0.13) eV. For these crystals we studied the valency shift of NdL_α line for crystals grown by different technology. VS for the Nd L_α line is (0.86±0.28) eV. The value of the shift depends on the growth conditions, the concentration of impurities and the thermal treatment. We may say that the conclusion about the formation of Nd^{+2} ions in definite garnet and perovskite crystals is correct.

The electronic states of ions in solid states may be discussed in approach of discrete (HFP approach for clusters) or effective occupation numbers approximations [6]. In first case we determinated the concentrations of ions of different electronic state (mixed valency). For example, concentration of Nd^{+2} ions in $Y_3Al_5O_{12}$ or $YAlO_3$ crystals may be calculated by the following formula

$$C(\mathrm{Nd}^{+2}) = (E_{\mathrm{exp}} - E_0)/E_{\mathrm{theor}} \cdot 100\% \tag{5}$$

where E_{exp} is NdL_α line energy for examined sample, E_0 is the energy of this line for a etalon sample and E_{theor} is the theoretical value of VSXL [6]. For investigated crystals values of $C(Nd^{+2})$ change from 8 to 22%, approximatelly. Theoretical foundations, mathematical procedure and numerical results for a lot of clusters $RA^{+n}:[L]_k$-cluster, where L is a ligand and k the number of ligands under different values of intra-atomic distance were obtained in Refs. [5,6].

For a second method we are using Exp. (4) for effective occupation number (or effective charge of ion). In this approximation the value of effective charge of Nd ions in $Y_3Al_5O_{12}$ crystals change from 3 to 2.6. This value corresponds to the result of ab initio calculations in self-consistent approximation for clusters with high accuracy [10].

5. Conclusion

Study of the electronic structure, energy of X-ray lines of nf-ions, on the one hand, and detailed investigation of the influence of irradiation or thermal treatment on doped oxide crystals on the other hand, permit one to make a simple conclusion: the stability of the electronic state of the impurity is determined by the relation of the values of electrons ionization energy and Madelung's constant for cations site [5].

Results of the investigation of the electronic states of ions in crystals using the method of the valency shift of X-ray lines are the best for all our samples. For regular ions we obtained the limit of value of relative concentration of ions which have been changed valency in order to 5–10%. For an impurity this value is 5–7% for concentrations of doped ions 0.1–10 wt.% and 10–30% for an impurity concentration of −0.005–0.1 wt.%.

These results are necessary for different investigations of stationary and short-time processes in plasma, galaxy and solid states. The Hartree–Fock–Pauli procedure which was used here gives the energy of X-ray lines with 0.5–1.5% accuracy. For K, L_α and L_β lines the deviation of our results from experimental data [15] are 0.5–2.6%. The reason of this deviation can be the simplification in the theoretical foundations and, also, systematic experimental errors. We believe that close comparison of the theoretical and experimental data can be done in future.

References

[1] C. Froese-Fischer, The Hartree–Fock Method for Atoms, Wiley, New York, 1977.

[2] J.C. Morrison, Many-Body Atomic Calculations, Springer, New York, 1987.

[3] R.D. Cowan, The Theory of Atomic Structure and Spectra, Univ. California Press, Berkely, 1981.
[4] B.G. Wybourne, Spectroscopic Properies of Rare Earth, Wiley, New York, 1965.
[5] N.A. Kulagin, D.T. Sviridov, The Methods of Electronic Structure Calculations for Free and Impurity Ions. Nauka, Moscow, 1986 (in Russian).
[6] N.A. Kulagin, D.T. Sviridov, Introduction to Doped Crystals Physics, High School. Publ, Kharkov, 1990, (in Russian).
[7] N.A. Kulagin, Sov. Opt. Spectr. 63 (1987) 964.
[8] N.A. Kulagin, I.I. Zalubovsky, J. Phys. B. 14 (1981) 1537.
[9] N.A. Kulagin, J. Phys. B 17 (1983) 1695.
[10] N. Kulagin, J. Phys. B 28 (1995) 373.
[11] O.I. Sumbaev, Sov. Usp. Fiz. Nauk. 124 (1978) 281.
[12] W.T. Carnall, Preprint ANL-85-8 Argonne, Nat. Lab, Illinois, 1985.
[13] J. Blaise, J.F. Wyart, J.G. Conway, E.F. Worden, Physica Scripta. 22 (1980) 224.
[14] G.K. Liu, V. Beitz, Phys. Rev. B41 (1990) 6201.
[15] J.P. Hessler, R. Brundage, J. Hegarty, W.M. Yen, Opt. Lett. 5 (1980) 348.
[16] A.E. Sandstrom, in: S. Flugge (Ed.), Encyclopedia of Physics, 1957, pp. 182–196.
[17] D. Hartree, Atomic Structure Calculations, Wiley, London, 1960.
[18] K. Vo Chiong, J. Zaitseva, N. Kulagin et al., Fiz. Tver. Tela. 26 (1984) 3521.
[19] N.A. Kulagin, M.F. Ozerov, Fiz. Tver. Tela. 35 (1993) 2472.
[20] N. Kulagin, D. Sviridov, J. Phys. C 17 (1984) 4539.