## ELECTRONIC STRUCTURE AND X-RAY SPECTRA OF THE Ce<sub>2</sub>ScSi<sub>2</sub> COMPOUND

I. D. Shcherba<sup>1</sup>, V. N. Antonov<sup>2</sup>, D. Uskokovic<sup>3</sup>, L. V. Bekenov<sup>2</sup>,

H. Noga<sup>4</sup>, M. V. Kovalska<sup>1</sup>, Z. M. Shpyrka<sup>1</sup>, V. A. Denys<sup>1</sup>

<sup>1</sup>Ivan Franko National University of Lviv,

8, Kyrylo & Mefodiy St., Lviv, UA-79005, Ukraine

<sup>2</sup>G. V. Kurdyumov Institute for Metal Physics of the N.A.S. of Ukraine,

UA-03142 Kyiv, Ukraine

<sup>3</sup>Institute of Technical Sciences of SASA,

Knez Mihailova 35/IV, PO Box 37711000 Belgrade, Serbia

 $^4$  Institute of Technology, Pedagogical University,

2, Podchorążych St., 30-084 Cracow, Poland

 $e\text{-}mail:\ ishcher ba@gmail.com$ 

(Received 28 August 2020; in final form 19 October 2020; accepted 22 October 2020; published online 01 December 2020)

X-ray absorption spectrum at the  $L_3$  edge of Ce and X-ray emission spectra at the K and  $L_{2,3}$  edges of Si in the mixed-valence compound Ce<sub>2</sub>ScSi<sub>2</sub> with the crystal structure of its own type have been studied experimentally and within the framework of the density functional theory with an additional Hubbard-like term (DFT+U). Good agreement between the theory and the experiment was found. Both the trivalent and the quadrivalent Ce ions in Ce<sub>2</sub>ScSi<sub>2</sub> are reflected in the experimentally measured Ce  $L_3$  X-ray absorption spectrum, simultaneously. We have found that the valence of cerium in Ce<sub>2</sub>ScSi<sub>2</sub> corresponds to approximately 92% of cerium ions in 3<sup>+</sup> state and 8% of them in 4<sup>+</sup> state. The obtained results suggest existence of the fluctuating transition "state-of-intermediate-valence (SIV)–Kondo-syste" in the Ce<sub>2</sub>ScSi<sub>2</sub> compound.

Key words: X-ray spectra, mixed valence, electronic structure, intermetallides.

DOI: https://doi.org/10.30970/jps.24.4702

#### I. INTRODUCTION

In rare earth compounds, where 4f levels are relatively close to the Fermi energy, various anomalous phenomena frequently appear. Most of them can be attributed to the hybridization between the 4f states and conduction bands. A mixed-valence (MV) state is one of these phenomena. The MV phenomenon has attracted a great deal of interest during the last several decades in connection with valence fluctuations [1-5]. In the gas phase most rare earths are divalent, but in the solid state most are trivalent, due to the large cohesive energy gained by promoting a 4f electron into an extended bonding state. The rare earth compounds based on Ce. Sm. Eu. Tm and Yb ions frequently exhibit a mixed-valence state consisting of divalent and trivalent valences [6–11]. In mixed-valence compounds, therefore, one must consider the charge degrees of freedom of the 4f ions in addition to the spin and orbital degrees of freedom.

It is necessary to distinguish between homogeneously mixed-valence compounds and inhomogeneously mixedvalence compounds. In the former, all the rare earth ions occupy crystallographically equivalent sites and therefore, this is essentially a single ion property where the magnetic ion hybridizes with the sea of the conduction electrons, causing an exchange of the inner 4f electron with the conduction band at the Fermi level. Such effects are expected to arise in systems where two electron configurations corresponding to 4f occupation numbers n and n-1 have nearly degenerate energies. So, the ground state of a homogeneously mixed valence compound is a quantum mechanical mixture of both the  $4f^n$  and the  $4f^{n-1}d$  configurations on each rare earth ion. Typical compounds exhibiting homogeneously mixed-valence phenomena are rare earth materials TmSe, SmS (high pressure golden phase), SmB<sub>6</sub>, YbB<sub>12</sub>, and YbInCu<sub>4</sub> [12].

In the case of inhomogeneously or static mixed-valence compounds, rare earth ions with different valence occupy clearly different sites. However, at high temperatures they become homogeneously mixed-valence semi-metals or valence fluctuating insulators. Their 4f electrons are strongly correlated and close to localization, i.e., having low effective kinetic energy. The 4f electrons can hop between the magnetic ions with different valence due to thermal activation (a thermal valence fluctuating state). If the intersite Coulomb repulsion is large enough it may dominate the kinetic energy and, once the chargedisorder entropy due to hopping is low enough, lead to a charge-ordered transition at a critical temperature Tco below which the valence fluctuation is suppressed. The resulting inhomogeneously mixed-valence state consists of two species of ions with the  $4f^n$  and the  $4f^{n-1}d$ configurations. This transition may be compared to the Wigner crystallization on a lattice [13], and its earliest example is the Verwey transition in magnetite  $Fe_3O_4$ [14], although this picture turned out to be too simplified for this compound [15, 16]. There are several chargefluctuating in-homogeneous mixed-valence compounds containing rare earth ions. They are the rare earth pnictides Yb<sub>4</sub>As<sub>3</sub>, Sm<sub>4</sub>Bi<sub>3</sub> and Eu<sub>4</sub>As<sub>3</sub> with the cubic anti- $Th_3P_4$  structure and rare earth chalcogenides  $Sm_3X_4$ (X = S, Se or Te) and  $Eu_3S_4$  with the  $Th_3P_4$  structure.

Compounds with the valence unstable ions R continue to be in the limelight especially compounds with

the Kondo lattice. There are reports about the structure of the valence and conduction bands of the ternary systems R-M-X, where M is, as a rule, a transition element of the Fe subgroup. Undoubtedly, the electron energy spectrum of the ternary compounds in which two components are rare-earth metals with the preservation of the trigonal-prismatic coordination for the X atom attracts considerable interest. The compound Ce<sub>2</sub>ScSi<sub>2</sub> is one of the brightest representatives of such class of intermetallides.

Compounds without a transition element of the Fe subgroup are also interesting in terms of XPS spectra interpretation. Because of the equality of the values of the photoionization cross-sections of the electron shells of R and Si, the fine structure of their valence band spectrum is considerably richer, which provides more reliable information about the electron-energy spectrum.

The most important characteristic of the valence instability of rare earth ions in intermetallides is the occupancy of 4f states and its variation as a function of composition and temperature. On this basis, the identification of valence states becomes exceptionally significant. The basic method for the determination of the valence of rare earths is the X-ray absorption spectroscopy. The aim of this paper is the experimental and ab initio theoretical study of the electronic structure and X-ray absorption and emission spectra of the Ce<sub>2</sub>ScSi<sub>2</sub> compound.

# II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

#### A. Crystal structure and experimental details

The crystal structure of the ternary Ce<sub>2</sub>ScSi<sub>2</sub> compound was investigated by means of X-ray powder diffraction [17]. The compound is a superstructure of the type U<sub>3</sub>Si<sub>2</sub>, space group P4/mbm,  $a = 7.61 \pm 0.01$  Å,  $c = 4.402 \pm 0.003$  Å. Four cerium atoms occupy the 4hsites, two scandium atoms occupy 2a sites, and silicon atoms occupy 4g sites. The unit cell and coordination polyhedra of the Ce<sub>2</sub>ScSi<sub>2</sub> atoms are shown in Fig. 1. The interatomic distances and coordination numbers of the atoms in Ce<sub>2</sub>ScSi<sub>2</sub> are presented in Table 1. The Ce<sub>2</sub>ScSi<sub>2</sub> compound can be considered as a combination of tetragonal [ScCe<sub>8</sub>] columns and dual trigonal prisms [ScCe<sub>6</sub>], which are the fragments of the CsCl and AlB<sub>2</sub> structural types, respectively.

As starting materials to produce  $Sc_{20}Ce_{40}Si_{40}$  alloys we used scandium, cerium and silicium, all with a nominal purity greater than 99.9 wt%. The samples each of a total mass of about 1 g were prepared by the arc melting of pure metals in a high-purity argon atmosphere. The mass loss after the melting was less than 1 wt%. After the melting the samples were sealed in evacuated quartz ampoules and annealed at 600°C for 720 hours. After annealing the ampoules were quenched in cold water. The phase analysis of the samples was carried out with the use of powder X-ray diffraction (XRD) (DRON-4.0M with FeK $\alpha$  radiation).



Fig. 1. The projection of the unit cell of  $Ce_2ScSi_2$  on the XY plane and the coordination polyhedra of Ce, Sc and Si atoms

Atoms	Distance,	nm	Coordination	numbers
Ce-4 Ce	0.397			
Ce	0.381			
$2 { m Ce}$	0.440		17	
$4~{ m Sc}$	0.356			
$2 \mathrm{Si}$	0.315			
4 Si	0.316			
Sc-8 Ce	0.356			
$2~{ m Sc}$	0.440		14	
$4~{ m Si}$	0.307			
Si–2 Ce	0.315			
$4~{\rm Ce}$	0.316		9	
$2~{ m Sc}$	0.307			
Si	0.243			

Table 1. The interatomic distances and coordination numbers of the atoms in the Ce<sub>2</sub>ScSi<sub>2</sub>. Atomic radii: Ce - 0.181 nm, Sc - 0.164 nm, Si - 0.134 nm

The absorption Ce  $L_3$  and emission Si K spectra in the ternary  $Ce_2ScSi_2$  compound were obtained at 300 K using a tube spectrometer equipped with an RKD-01 coordinate detector of original design as described in our previous publications [18, 19]. Quartz crystals (1010; radius of curvature 2.0 m) were used as the crystal analyzer. The instrumental broadening for the Si Kspectra was equal to 0.2 eV. The Si  $L_{2,3}$  spectra were measured with the SARF spectrometer using a mica crystal (001) as the crystal analyzer. The spectra of the core levels and the valence band were measured by the "Kratos" X-ray photoelectron spectrometer (the Institute for Metal Physics of the N.A.S. of Ukraine). The  $K\alpha\text{-line}$  of Mg with the energy of 1253.6 eV served as a photon source. The spectrometer resolution was 0.9 eV, and the precision of positioning the core levels maxima was 0.1 eV.

#### B. Computational details

The *ab initio* theoretical study was performed using the spin-polarized fully relativistic linear-muffin-tinorbital (SPR LMTO) method for the experimentally observed lattice constants [20–22]. The basis consisted of the Ce *s*, *p*, *d*, and *f*; Sc *s*, *p*, *d* and *f*; Si *s*, *p*, and *d* LMTO's. The *k*-space integrations were performed using the improved tetrahedron method [23] and the selfconsistent charge density was obtained with 252 irreducible *k*-points.

The X-ray absorption and emission spectra were calculated considering the exchange splitting of core levels. The finite lifetime of a core hole was accounted for by folding the spectra with a Lorentzian. The widths of the core level spectra were taken from literature [24]. The finite resolution of the spectrometer was accounted for by a Gaussian.

In order to simplify the comparison of the theoretical X-ray isotropic absorption Ce  $L_3$  spectrum of Ce<sub>2</sub>ScSi<sub>2</sub> to the experimental one, we take into account the background intensity, which effects the high energy part of the spectra and is caused by a different kind of inelastic scattering of the electron promoted to the conduction band above the Fermi level due to X-ray absorption (scattering on the potentials of surrounding atoms, defects, phonons etc.). To calculate the background spectra, we used the model proposed by Richtmyer *et al.* [25]. The absorption coefficient for the background intensity is

$$\mu(\omega) = \frac{C\Gamma_c}{2\pi} \int_{E_{cf_0}}^{\infty} \frac{dE_{cf}}{\left(\frac{\Gamma c}{2}\right)^2 - (\hbar\omega - E_{cf})^2},\qquad(1)$$

where  $E_{cf} = E_c - E_f$ ,  $E_c$  and  $\Gamma_c$  are the energy and the lifetimes broadening of the core hole,  $E_f$  is the energy of the empty continuum level,  $E_{cf_0}$  is the energy of the lowest unoccupied continuum level, and C is a normalization constant which is used as an adjustable parameter in this paper.

To treat the strong on-site Coulomb interaction of localized Ce 4f electrons, we used the "relativistic" generalization of the GGA+U method, which takes into account the spin-orbit coupling so that the occupation matrix of localized electrons becomes non-diagonal in spin indexes [26]. The screened on-site Coulomb U and exchange J integrals enter the GGA+U energy functional as external parameters and have to be determined independently. Our constrained LSDA calculations produced J = 0.9 eV at the Ce site in Ce<sub>2</sub>ScSi<sub>2</sub>, and for U we used the value U = 6.0 eV, which is typical of Ce systems.

#### **III. RESULTS AND DISCUSSION**

#### A. Electronic structure

Figure 2 presents partial density of states of  $Ce_2ScSi_2$ calculated using the GGA+U approach. For the Ce ion we found a magnetic solution with an occupied 4f spinup electron band situated below the Fermi level in the energy range between -2.8 and -1.0 eV and empty 4fbands above the Fermi level between 1.0 and 5.8 eV.



Fig. 2. Partial density of states of  $Ce_2ScSi_2$ [in states/(atom eV)]

The Sc 3d states are situated in the range from -3.8 eV to 8.3 eV. The Si 3p states occupy mainly the energy interval from -3.9 to 8.3 eV and hybridize well with Sc 3d states. The Si 3s states are situated in the range between -9.0 eV and -8.0 eV and at -6.1 eV.

# B. XPS spectrum of the valence band of the $R_2$ ScSi<sub>2</sub> compound (R = La, Ce). X-ray absorption and emission spectra

In the XPS spectrum of the valence band of the  $ScR_2Si_2$  compounds (R = La, Ce) (Fig. 3) two groups of maxima are observed with binding energies of  $\sim 2 \text{ eV}$  and 6–12 eV, respectively.

The maximum near the Fermi level is caused mainly by a contribution of the 4f electrons of Ce and 3p states of Si. The matching of the singularity at 7 eV with the main maximum of the Si  $L_{2,3}$  band (Fig. 4) explains the manifestation of the Si 3s states in the XPS spectrum.

At the same time, as can be concluded from the data (Table 2), the energies of the Ce  $3d_{5/2}$  and Sc  $2p_{3/2}$  levels increase compared with pure components, suggesting a preference for the formation of Si–Si bonds.

$\operatorname{Compound}$	Si 2 $p_{3/2}$ , eV	Sc $2p_{3/2}$ , eV	Ce $3d_{5/2},\mathrm{eV}$
${\rm Ce_2ScSi_2}$	98.6	399.2	883.8
Si, Ce, Sc	99.1	399.0	883.6

Table 2. Energies of core levels of components in ternary silicide

The states of intermediate valence (SIV) in metallic systems can be seen in the thermal emf as a considerable positive part with an extremum  $T\alpha_{\rm max} = \Gamma$  ( $\Gamma$  is the width of the  $\rho(E_{\rm F})$  peak) [27, 28]. A qualitative comparison of  $\alpha(T)$  of Ce<sub>2</sub>ScSi<sub>2</sub> and its structural analog ScLa<sub>2</sub>Si<sub>2</sub> implies the presence of such part at  $T\alpha_{\rm max} =$ 100–150 K (Fig. 5). This can correspond to a state of Ce in the region of the "SIV–Kondo-system" transition, i. e. to a state with almost integer valence of Ce.



Fig. 3. XPS spectrum of the valence electrons of Ce in the Ce<sub>2</sub>ScSi<sub>2</sub> and La<sub>2</sub>ScSi<sub>2</sub> compounds

The  $L_3$  absorption spectroscopy enables determination of the R ions valence with sufficient accuracy. The  $L_3$  absorption spectrum of cerium in Ce<sub>2</sub>ScSi<sub>2</sub> (Fig. 6) demonstrates a clearly expressed maximum corresponding to the  $4f^{1}5d^{1}6s^{2}$  electron configuration and another one of low intensity at 7.5 eV, which reflects the existence of the Ce $4f^{0}5d^{2}6s^{2}$  configuration. The calculation of the valence of cerium in Ce<sub>2</sub>ScSi<sub>2</sub> (3.08 ± 0.02) shows that it just insignificantly differs from the integer one in the ScCeSi compound. The results obtained by the absorption spectroscopy are in good agreement with the XPS spectra of the Ce 3d core levels in these compounds

The dependence of the magnetic susceptibility  $\chi(T)$ of the Ce<sub>2</sub>ScSi<sub>2</sub> compound within a wide temperature range corresponds to the Curie–Weiss law (Fig. 7). The determined local magnetic moment at Ce site in Ce<sub>2</sub>ScSi<sub>2</sub> is 2.38 $\mu_{\rm B}$ , which is smaller compared to the theoretical value of 2.5 $\mu_{\rm B}$  for Ce<sup>3+</sup> in a regular magnetic state.



Fig. 4. Theoretical and experimental Si K and Si  $L_{2,3}$  spectra for  $Ce_2ScSi_2$ 



Fig. 5. Temperature dependence  $\alpha(T)$  for the ScLa<sub>2</sub>Si<sub>2</sub> and Ce<sub>2</sub>ScSi<sub>2</sub> compounds



Fig. 6. Theoretical (full line) and experimental (circles)  $L_3$ X-ray absorption spectra of Ce in Ce<sub>2</sub>ScSi<sub>2</sub>. The dotted line shows the theoretical background spectrum



Fig. 7. The temperature dependence of the magnetic susceptibility  $\chi(T)$  for the Ce<sub>2</sub>ScSi<sub>2</sub> compound

We can conclude that the obtained results suggest existence of the fluctuating transition of the type "SIV-Kondo-system" in the Ce<sub>2</sub>ScSi<sub>2</sub> compound.

#### IV. CONCLUSIONS

We have studied experimentally and theoretically the electronic structure, X-ray emission spectra of Si at the K and  $L_{2,3}$  edges and X-ray absorption spectrum at the Ce  $L_3$  edge in the mixed valent compound Ce<sub>2</sub>ScSi<sub>2</sub>. The calculations show good agreement with the experimental measurements.

It has been found that the structure of the valence band of the  $Ce_2ScSi_2$  compound considerably differs from that of the similar compounds with 3d transition elements by the absence of high electron density at the Fermi level. The near Fermi region of the occupied part of the valence band is formed by the 4f states of Ce and 3d states of Sc. The middle of the valence band is occupied by the p states of Si. At the bottom of the valence band, the 3s states of silicon are dominating.

We have found that the valence of cerium in  $Ce_2ScSi_2$ corresponds to approximately 92% of cerium ions in 3<sup>+</sup> state and 8% of them in 4<sup>+</sup> state. The obtained results suppose existence of the fluctuating transition "SIV– Kondo-system" in the  $Ce_2ScSi_2$  compound.

- [1] C. M. Varma, Rev. Mod. Phys. 48, 219 (1976); https: //doi.org/10.1103/RevModPhys.48.219.
- J. M. Lawrence, P. S. Riseborough, R. D. Parks, Rep. Prog. Phys. 44, 1 (1981); https://doi.org/10.1088/00 34-4885/44/1/001.
- [3] P. Wachter, in Handbook of the Physics and Chemistry of Rare Earths. Lanthanides/Actinides: Physics - II. Vol. 19, edited by K. A. Gschneidner, Jr., LeRoy Eyring G. H. Lander, G. R. Choppin (Elsevier, 1994), p. 177; https: //doi.org/10.1016/S0168-1273(05)80061-3.
- [4] V. Antonov, B. Harmon, A. Yaresko, Electronic Structure and Magneto-Optical Properties of Solids (Kluwer, Dordrecht, 2004).
- [5] T. Goto, B. Lüthi, Adv. Phys. 52, 67 (2003); https: //doi.org/10.1080/0001873021000057114.
- [6] Y. Kishimoto, Y. Kawasaki, T. Ohno, Phys. Lett. A 317, 308 (2003); https://doi.org/10.1016/j.physleta.200 3.08.050.
- [7] C. L. Chang, C. L. Dong, C. L. Huang, Y. Y. Chen, J. Appl. Phys. 87, 149 (2000); https://doi.org/10.1063/ 1.372347.
- [8] B. L. Drake *et al.*, J. Phys.: Condens. Matter 22, 426002 (2010); https://doi.org/10.1088/0953-8984/ 22/42/426002.
- [9] V. H. Tran, J.-C. Griveau, R. Eloirdi, E. Colineau, Phys. Rev. B 89, 054424 (2014); https://doi.org/10.1103/ PhysRevB.89.054424.
- [10] Y. Utsumi et al., Phys. Rev. B 86, 115114 (2014); https: //doi.org/10.1103/PhysRevB.89.115114.
- [11] T. Toliński, A. Kowalczyk, M. Pugaczowa-Michalska, G. Chełkowska, J. Phys.: Condens. Matter 15, 1397 (2003); https://doi.org/10.1088/0953-8984/15/9/3 03.
- [12] V. N. Antonov, L. V. Bekenov, A. N. Yaresko, Adv. Cond. Matter Phys. 2011, 298928 (2011); https://do

i.org/10.1155/2011/298928.

- [13] P. Fulde, Ann. Phys. 509, 178 (1997); https://doi.or g/10.1002/andp.19975090303.
- [14] E. J. W. Verwey, P. W. Haayman, Physica 8, 979 (1941); https://doi.org/10.1016/S0031-8914(41)80005-6.
- [15] V. N. Antonov, B. N. Harmon, V. P. Antropov, A. Y. Perlov, A. N. Yaresko, Phys. Rev. B 64, 134410 (2001); https://doi.org/10.1103/PhysRevB.6 4.134410.
- [16] I. Leonov, A. N. Yaresko, V. N. Antonov, M. A. Korotin, V. I. Anisimov, Phys. Rev. Lett. 93, 146404 (2004); ht tps://doi.org/10.1103/PhysRevLett.93.146404.
- [17] O. I. Bodak, I. R. Mokra, in: Proc. of the III All-Union Conference on Crystal Chemistry of Intermetallic Compounds (Vyshcha shkola, Lviv, 1978), p. 66.
- [18] I. D. Shcherba em et al., J. Electron Spectrosc. Relat. Phenom. 131, 125 (2003); https://doi.org/10.1016/ S0368-2048(03)00127-0.
- [19] I. D. Shcherba, V. M. Antonov, B. Ya. Kotur, J. Alloys Compd. 242, 58 (1996); https://doi.org/10.1016/09 25-8388(96)02335-3.
- [20] O. K. Andersen, Phys. Rev. B 12, 3060 (1975); https: //doi.org/10.1103/PhysRevB.12.3060.
- [21] V. V. Nemoshkalenko *et al.* Phys. Status Solidi B **120**, 283 (1983); https://doi.org/10.1002/pssb.222120013 0.
- [22] V. N. Antonov, A. Y. Perlov, A. P. Shpak, A. N. Yaresko, J. Magn. Magn. Mater. 146, 205 (1995); https://doi. org/10.1016/0304-8853(95)01083-1.
- [23] P. E. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49, 16223 (1994); https://doi.org/10.1103/PhysRevB .49.16223.
- [24] J. L. Campbell, T. Parr, At. Data Nucl. Data Tables 77, 1 (2001).
- [25] F. K. Richtmyer, S. W. Barnes, E. Ramberg, Phys. Rev.

64, 843 (1934); https://doi.org/10.1103/PhysRev.46 .843.

[27] M. Koterlin, B. Morokhivski, I. Shcherba, J. Serb. Chem. Soc. 56, 733 (1991).

[26] A. N. Yaresko, V. N. Antonov, P. Fulde, Phys. Rev. B 67, 155103 (2003); https://doi.org/10.1103/Phys RevB.67.155103. [28] N. B. Brandt, V. V. Moshchalkov, Adv. Phys. 33, 193 (1984); https://doi.org/10.1080/00018738400101661

### ЕЛЕКТРОННА СТРУКТУРА ТА Х-ПРОМЕНЕВІ СПЕКТРИ СПОЛУКИ Се $_2ScSi_2$

I. Д. Щерба<sup>1</sup>, В. М. Антонов<sup>2</sup>, Д. Узкович<sup>3</sup>, Л. В. Бекенов<sup>2</sup>, Г. Нога<sup>4</sup>,

М. В. Ковальська<sup>1</sup>, З. М. Шпирка<sup>1</sup>, В. А. Денис<sup>1</sup>

<sup>1</sup>Львівський національний університет імені Івана Франка,

<sup>2</sup> Інститут металофізики імені Г. В. Курдюмова НАНУ,

<sup>3</sup> Інститут технічних наук САНМ, вул. Князя Михаілова, 35/IV, Белград, 37711000, Сербія,

<sup>4</sup> Інститут техніки, Педагогічний університет, вул. Підхоронжих, 2, Краків, 30-084, Польща

Проведені експериментальні та теоретичні дослідження Х-променевих K і  $L_{2,3}$  спектрів випромінювання Si та  $L_3$  спектра поглинання Ce в сполуці зі змішаною валентністю Ce<sub>2</sub>ScSi<sub>2</sub>, що має кристалічну структуру власного типу. Теоретичні дослідження здійснені в межах теорії функціонала густини з додатковим членом, подібним до габбардівського (DFT+U). Установлено, що теорія й експеримент добре узгоджуються. В експериментально виміряному Х-променевому  $L_3$  спектрі поглинання Ce в Ce<sub>2</sub>ScSi<sub>2</sub> одночасно відображаються як тривалентні, так і чотиривалентні йони Ce. Ми виявили, що найліпше узгодження експериментального спектра з сумою теоретично розрахованих спектрів йонів Ce<sup>3+</sup> та Ce<sup>4+</sup> досягається за 92% йонів церію в стані 3<sup>+</sup> та 8% йонів у стані 4<sup>+</sup>. На основі аналізу енергій остових рівнів зроблено висновок (енергії рівнів Ce  $3d_{5/2}$  та Sc  $2p_{3/2}$  зростають порівняно з чистими компонентами) про тяжіння до утворення зв'язків Si–Si.

Методом фотоелектронної спектроскопії одержано енерґетичний спектр валентної зони та проведено суміщення з емісійними спектрами кремнію. У спектрі валентної зони сполук ScR<sub>2</sub>Si<sub>2</sub> (R = La, Ce) спостерігаємо дві групи максимумів з енерґіями зв'язку ~2 еВ та 6–12 еВ відповідно. Максимум поблизу рівня Фермі зумовлений здебільшого внеском 4f електронів Ce та 3p станів Si. Відповідність особливості за 7 еВ з основним максимумом смуги Si  $L_{2,3}$  пояснює прояв станів Si 3s у фотоелектронному спектрі. Одержано температурну залежність  $\alpha(T)$  для сполук ScLa<sub>2</sub>Si<sub>2</sub> та Ce<sub>2</sub>ScSi<sub>2</sub>. Залежність  $\chi(T)$  сполуки Ce<sub>2</sub>ScSi<sub>2</sub> в широкому діапазоні температур відповідає закону Кюрі–Вайса. Визначений локальний магнітний момент Ce у сполуці  $\mu$  Ce<sub>2</sub>ScSi<sub>2</sub> становить 2.38 $\mu_{\rm B}$ , що менше порівняно з теоретичним значенням  $2.5\mu_B$  для Ce<sup>3+</sup> в магнітному стані.

Отримані результати свідчать про наявність у сполуці Ce<sub>2</sub>ScSi<sub>2</sub> флуктувального переходу "стан проміжної валентності (СПВ)-система Кондо".

Ключові слова: рентґенівські спектри, змішана валентність, електронна структура, інтерметаліди.

вул. Кирила і Мефодія, 8, Львів, 79005, Україна,

просп. Вернадського, 36, Київ, 03142, Україна,