X -RAY SPECTRA, ELECTRON STRUCTURE AND PHYSICAL PROPERTIES OF THE Ce_2ScSi_2 COMPOUND

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Abstract

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_2ScSi_2 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_2ScSi_2 are reflected in the experimentally measured Ce L_3 x-ray absorption spectrum, simultaneously. We have found that the best agreement between the experimental spectrum and the sum of the theoretically calculated Ce^{3+} and Ce^{4+} spectra is achieved with 84% of cerium ions in 3^+ state and 16% of ions in 4^+ state. The obtained results suppose existence of the fluctuating transition "state-of-intermediate-valence (SIV) − Kondo-system" in the Ce_2ScSi_2 compound.

Keywords: x-ray spectra, mixed valence, electronic structure

1. 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 mixed-valence 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 $4f^{n-1}d$ configuration on each rare earth ion. Typical compounds exhibiting homogeneously mixed-valence phenomena are rare earth materials TmSe, SmS (high pressure golden phase), SmB_6, YbB_{12}, and $YbInCu_4$ [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 a 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 charge-disorder entropy due to hopping is low enough, lead to a charge-ordered transition at a critical temperature T_{co} 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 charge-fluctuating in-homogeneous mixed-valence compounds containing rare earth ions. They are the rare earth pnictides Yb_4As_3, Sm_4Bi_3 and Eu_4As_3 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 hold the limelight in the attention of scientists, 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 preservation of the trigonal-prismatic coordination for the X atom attracts considerable interest. The compound Ce_2ScSi_2 is one of the brightest representatives of such class of intermetallides.

Compounds without a transition element of the Fe subgroup are also interesting from the point of view of XPS spectra interpretation. Because of 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_2ScSi_2 compound.

2. Experimental and computational details

2.1. Crystal structure and experimental details

The crystal structure of the ternary Ce_2ScSi_2 compound was investigated by means of x-ray powder diffraction [17]. The compound is a superstructure of the type U_3Si_2, space group $P4/mbm$, $a = 7.61 \pm 0.01$ Å, $c = 4.402 \pm 0.003$ Å. Four cerium atoms

occupy the $4h$ sites, two scandium atoms occupy $2a$ sites, and silicon atoms occupy $4g$ sites. The unit cell and coordination polyhedra of the Ce_2ScSi_2 atoms are shown in Fig. 1. The interatomic distances and coordination numbers of the atoms in Ce_2ScSi_2 are presented in Table 1. The Ce_2ScSi_2 compound can be considered as a combination of tetragonal $[ScCe_8]$ columns and dual trigonal prisms $[ScCe_6]$, which are the fragments of the CsCl and AlB_2 structural types, respectively.
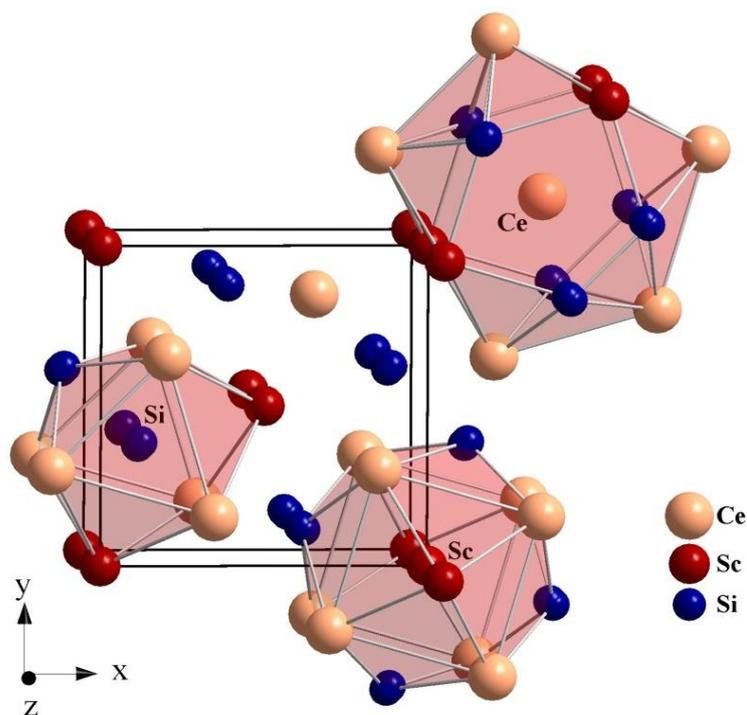

Fig. 1. The projection of the unit cell of Ce_2ScSi_2 on the XY plane and the coordination polyhedra of Ce, Sc and Si atoms.

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 FeKα radiation).

Table 1. The interatomic distances and coordination numbers of the atoms in the Ce_2ScSi_2 compound. Atomic radii: Ce – 0.181 nm, Sc – 0.164 nm, Si – 0.134 nm.

Atoms	Distance, nm	Coordination numbers
Ce – 4 Ce	0.397	
Ce	0.381	
2 Ce	0.440	17
4 Sc	0.356	
2 Si	0.315	
4 Si	0.316	
Sc – 8 Ce	0.356	
2 Sc	0.440	14
4 Si	0.307	
Si – 2 Ce	0.315	
4 Ce	0.316	9
2 Sc	0.307	
Si	0.243	

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 K spectra 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 Kα–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.

2.2. Computational details

The ab initio theoretical study was performed using the spin-polarized fully relativistic linear-muffin-tin-orbital (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 with the improved tetrahedron method [23] and the self-consistent 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_2ScSi_2 to the experimental one we take into account the background intensity which effects the high energy part of the spectra and is caused by different kind of inelastic scattering of the electron promoted to the conduction band above Fermi level due to x-ray absorption (scattering on 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

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

where $E_{cf} = E_c - E_f$, E_c and Γ_c are the energy and the lifetimes broadening of the core hole, E_f is the energy of 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_2ScSi_2, and for *U* we used the value $U = 6.0$ eV, which is typical for Ce systems.

3. Results and discussion

3.1. Electronic structure

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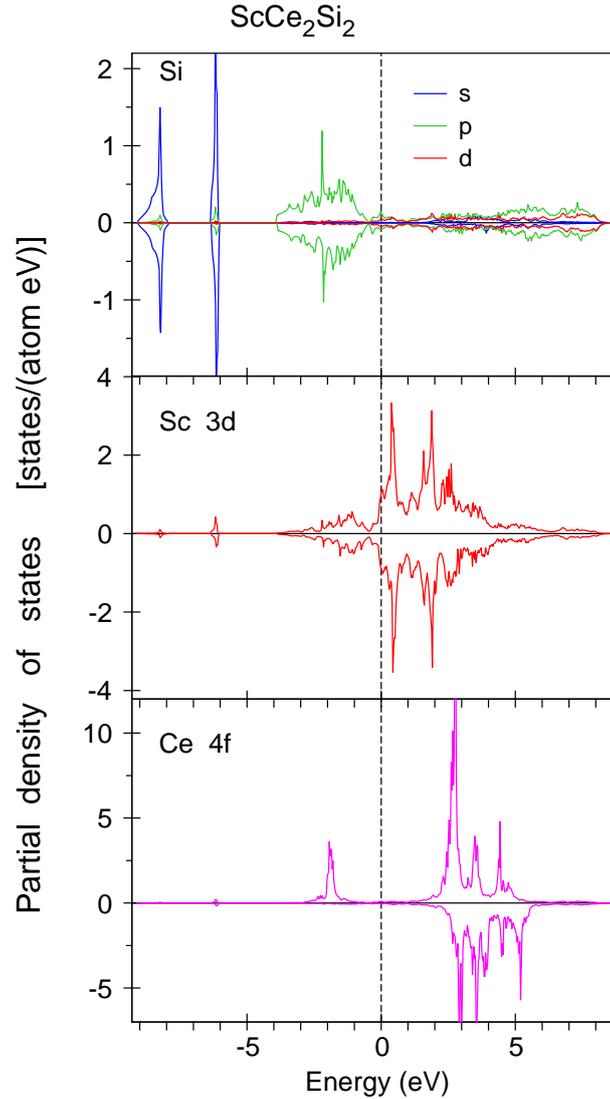

Fig. 2. Partial density of states of Ce_2ScSi_2 (in states/ (atom eV)).

The Sc 3d states are situated 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 between −9.0 eV and −8.0 eV and at −6.1 eV.

3.2. XPS spectrum of the valence band of the R_2ScSi_2 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 ~2 eV and 6-12 eV, respectively.
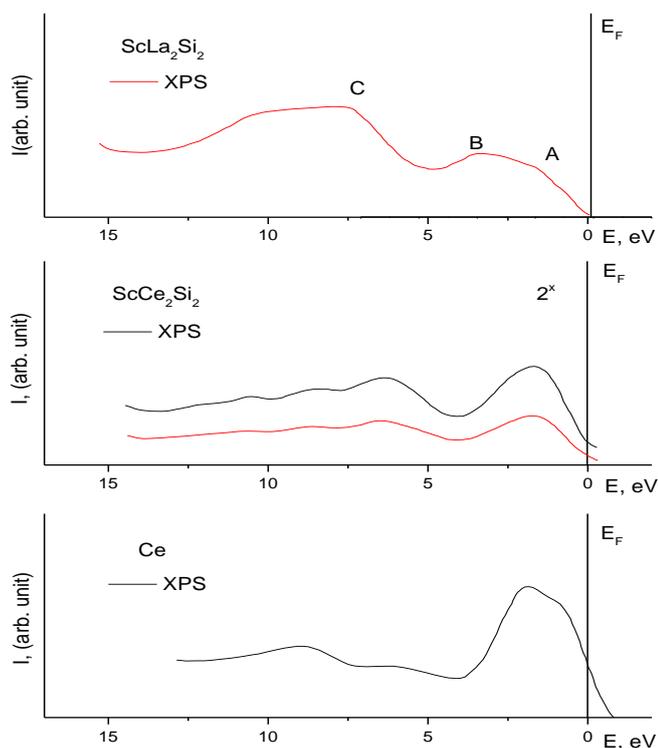

Fig. 3. XPS spectrum of the valence electrons of Ce in the Ce_2ScSi_2 and La_2ScSi_2 compounds.

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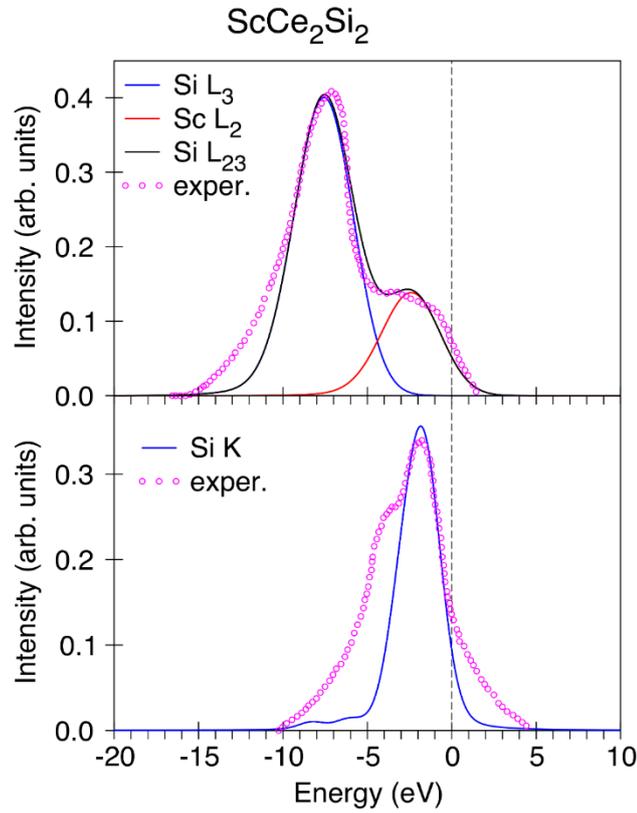
Fig. 4. Theoretical and experimental Si K and Si $L_{2,3}$ spectra for Ce_2ScSi_2.

At the same time, as can be concluded from the data (Table 2), the energy of the $3d_{5/2}$ level of Ce increases and that of the Sc $2p_{3/2}$ level remains practically unchanged as compared with pure components, suggesting a preference to the formation of bonds of the Si–Si interaction.

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

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

The states of intermediate valence (SIV) in metallic systems can be seen in the thermal emf as a considerable positive part with an extremum $T\alpha_{max} = \Gamma$ (Γ is the width of the $\rho(E_F)$ peak) [27,28]. A qualitative comparison of $\alpha(T)$ of Ce_2ScSi_2 and its structural analog $ScLa_2Si_2$ implies the presence of such part at $T\alpha_{max} = 100 - 150$ 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.
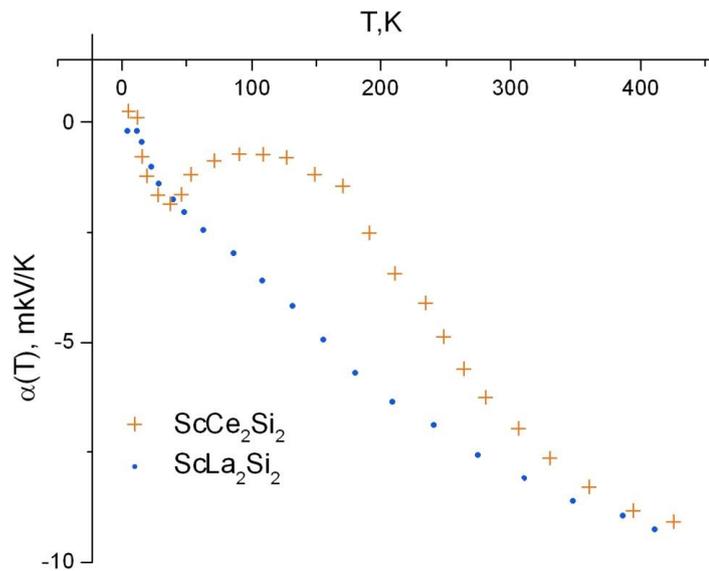
Fig. 5. Temperature dependence $\alpha(T)$ for the $ScLa_2Si_2$ and Ce_2ScSi_2 compounds.

The L_3 absorption spectroscopy enables determination of the R ions valence with enough accuracy. The L_3 absorption spectrum of cerium in Ce_2ScSi_2 (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 $Ce4f^0 5d^2 6s^2$ configuration. The calculation of the valence of cerium in Ce_2ScSi_2 (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.
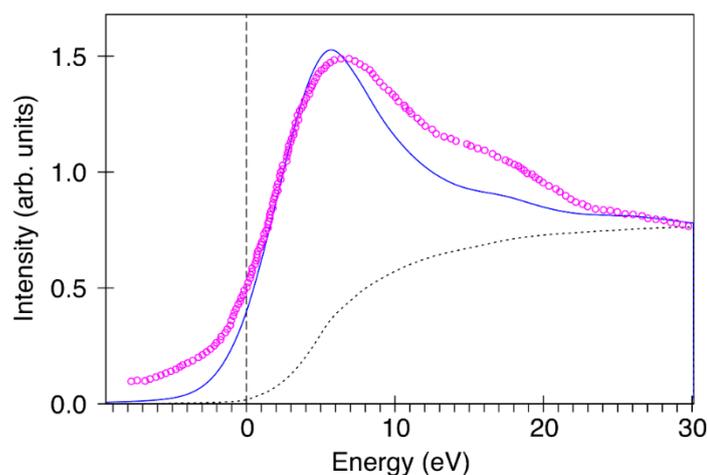

Fig. 6. Theoretical (full line) and experimental (circles) L_3 x-ray absorption spectra of Ce in Ce_2ScSi_2. The dotted line shows the theoretical background spectrum.

The dependence of the magnetic susceptibility $\chi(T)$ of the Ce_2ScSi_2 compound within a wide temperature range corresponds to the Curie-Weiss law (Fig. 7). The determined local magnetic moment at Ce site in Ce_2ScSi_2 is 2.38 μ_B, what is smaller compared to the theoretical value of 2.5 μ_B for Ce^{3+} in a regular magnetic state.

We can conclude that the obtained results suppose existence of the fluctuating transition of the type "SIV − Kondo-system" in the Ce_2ScSi_2 compound.
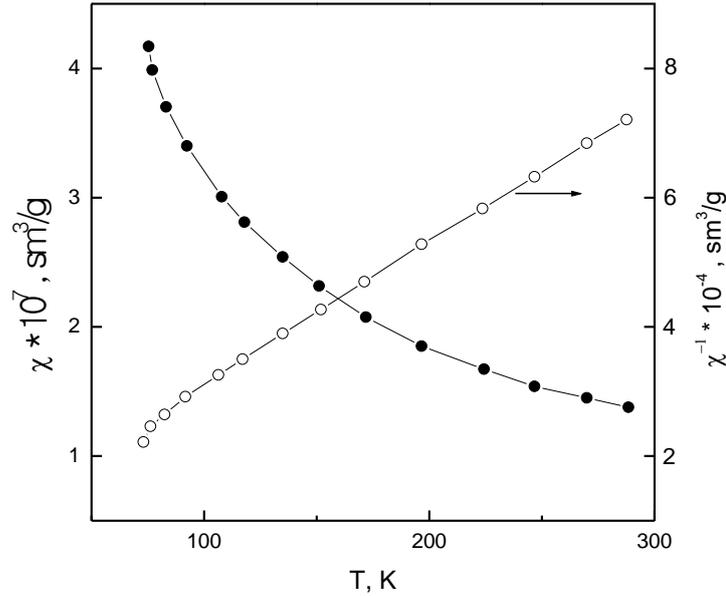

Fig. 7. The temperature dependence of the magnetic susceptibility $\chi(T)$ for the Ce_2ScSi_2 compound.

4. 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_2ScSi_2. 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 best agreement between the experimental spectrum and the sum of the theoretically calculated Ce^{3+} and Ce^{4+} spectra is achieved with 84% of cerium ions in 3+ state and 16% of ions in 4+ state. The obtained results suppose existence of the fluctuating transition "SIV−Kondo-system" in the Ce_2ScSi_2 compound.

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