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X-Ray and Mössbauer Spectra and Electronic Structure of $ScFe_2Si_2$ Compound

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Abstract: The valence band electronic structure of a compound with the $HfFe_2S_2$ crystal lattice type has been established for the first time based on X-ray emission spectroscopy measurements. Band structure and theoretical spectra of X-ray emission bands of atoms located in non-equivalent crystallographic positions are calculated by means of the LMTO method in non-relativistic approximation. A satisfactory agreement between theoretical and experimental data is achieved.^{57}Fe Mossbauer absorption measurements confirm iron atoms occupying non-equivalent positions in the crystal lattice.

Key words: Mossbauer spectroscopy, X-ray spectroscopy, electronic band structure, intermetallics.

1. Introduction

The $ScFe_2Si_2$ ternary intermetallic compound [1-3] has crystal lattice of the $HfFe_2Si_2$ structural type that belongs to a larger family of the ReM_2Si_2 silicides of the $CeGa_2Al_2$ [1, 4] structural type, where Re denotes rare-earth element M = Fe, Co, Ni, Cu. In this type of crystal lattice, the polyhedrons of Fe atoms have the same quantitative and qualitative composition, but are different in their structure. Fe2 atoms form lines parallel to z- axis with small Fe-Fe distance being equal to 2.509 Å, i.e. the same distance as in a-Fe (Fig. 1) [2]. Fe1 atoms contact only with Si2 atoms forming chains of quadrangles parallel to y-axis.

It is still not well understood why among more than 300 ternary intermetallic compounds ReM_2X_2, where M is transition d- element, X is sp-element (P, Al, Si, Ga, Ge), there are just two compounds with Sc and Hf that have a distinctive and unique crystal lattice where Fe and Si occupy two crystallographically non-equivalent positions. To reveal electronic structure as well as the type of chemical bonds in this particular family of the intermetallic compounds, we have conducted systematic X-ray spectroscopic investigations of the $ScFe_2Si_2$ compound. For the first time calculations of X-ray emission spectra have been conducted and the results are presented.

2. Details of Experiment and Theoretical Calculations

Samples of the $ScFe_2Si_2$ compound alloy were prepared by arc melting on a water-cooled copper hearth of pure constituent elements under pure argon atmosphere. The sample homogenization was conducted at temperatures of 800 °C unsealed under vacuum quartz ampoules for the duration of 350 h. The phase composition of the samples was analyzed by means of X-ray diffraction technique.

Obtained X-ray diffraction data were analyzed by a software package developed at National University of Lviv. Published crystal lattice coordinates [2] were used to calculate distances between atoms in the $ScFe_2Si_2$ structure. The resulting parameters (Table 1 and Table 2) agree well with available literature [1].

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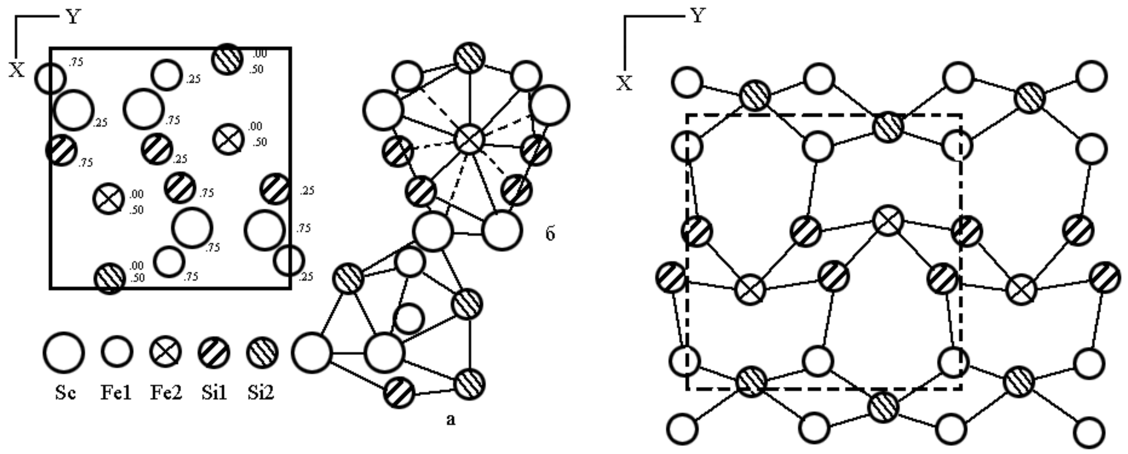


Fig. 1 Crystalline structure of $ScFe_2Si_2$.

Table 1 The structural characteristics of $ScFe_2Si_2$.

Compound	Space group	Lattice parameters of $ScFe_2Si_2$, nm		
		a	*b*	*c*
$ScFe_2Si_2$	Pbcm	0,7266(5)	0,7108(4)	0,5018(3)

a = 0,7266 nm, *b/a* = 0,974253, *c/a* = 0,68966.

Table 2 Nearest-neighbor distances in $ScFe_2Si_2$[*].

Distance	nm	Distance	nm
Si - Si	0,2891 (Si1-Si1) 0,2509 (Si2-Si2)	Fe - Fe	0,2509 (Fe2-Fe2)
Si - Fe	0,2255 (Si1-Fe1) 0,2292 (Si2-Fe1) 0,2411 (Si1-Fe2) 0,2460 (Si2-Fe1) 0,2480 (Si2-Fe2) 0,2493 (Si1-Fe2)	Sc - Si	0,2716 (Sc-Si2) 0,2779 (Sc-Si2) 0,2795 (Sc-Si1) 0,2828 (Sc-Si1)
		Sc - Fe	0,2763 (Sc-Fe1) 0,2839 (Sc-Fe1)

[*] Radius of atoms: Sc-0,164 nm, Fe-0,126 nm, Si-0,117nm-0,120 nm.

Atomic positions:

Component	x	y	z
Sc	0,2482	0,0981	0,25
Fe1	0,6173	0,25	0
Fe2	0,1176	0,4895	0,25
Si1	0,9493	0,25	0
Si2	0,417	0,449	0,25

The experimental setups for obtaining X-ray Fe and Si K- and L- emission spectra [5] and for the Mossbauer absorption measurements [6] were described elsewhere.

The calculations of electron energy bands E (k) and partial DOS (density of states) for $ScFe_2Si_2$ compound were performed by the semi-relativistic LMTO (linear muffin-tin orbital) method without taking into consideration spin-orbital interactions. The eigen values were calculated at 252 points within a 1/16 Brillion zone. The exchange potential of Barth and Hedin [7] was taken into account during the calculations.

3. Results and Discussion

The theoretically calculated X-ray emission valence bands and experimental ones of Fe and Si in $ScFe_2Si_2$ are matched in the unified energy scale and are shown in Figs. 2-5. As emission spectra from Sc atoms have an extremely low intensity, they can be obtained only with enormous efforts by a long time exposition [5]. Good agreement between the experimental and theoretical curves is observed for the K- and L bands of Fe. The presence of $K\beta''$-satellite, in general, indicates $4p \to 1s$ transition as the feature of Fe $K\beta_{2,5}$-band.

The main maximum C (Fig. 2) of the Si $L_{II,III}$-band (the $3s \to 2p$ transition) coincides in energy with the maximum F (Fe $K\beta''$-satellite) and indicates that there is a considerable contribution of the hybridized Si s-states to the intensity of Fe $K\beta_{2,5}$-band. The experimental Si $K\beta$-band (the $3p \to 1s$ transition) turns

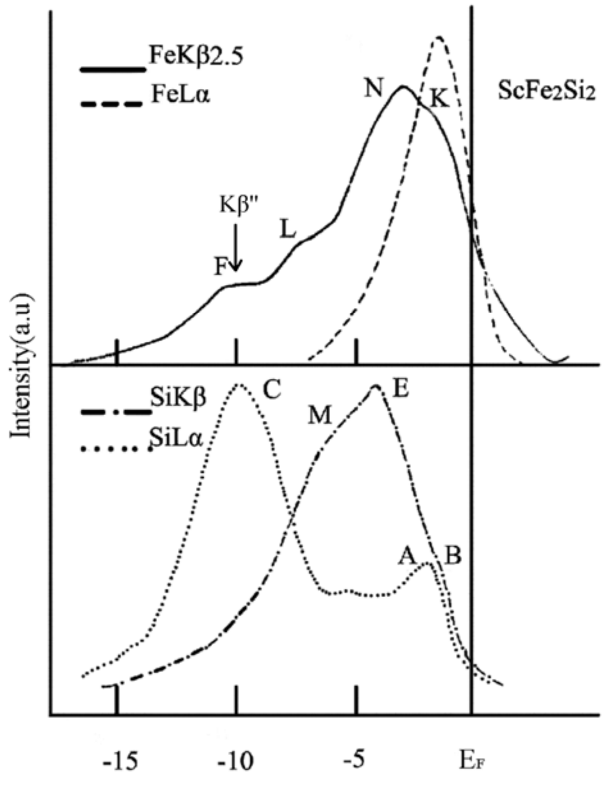


Fig. 2 Observed X-ray emission valence spectra of Fe and Si in ScFe$_2$Si$_2$ matched in the unified energy scale.

out to be wider (by half of its height) than the theoretical one. The maximum near the Fermi level which is typically observed for ternary compounds [5, 8, 9], and can be connected with contribution of the Fe3d-states.

As we noticed above, the structure under investigation differs from the known structural type CeGa$_2$Al$_2$, i.e. iron and silicon atoms have two crystallographically non-equivalent positions labelled in Fig. 1 as Fe1, Fe2, Si1, Si2, respectively. In such cases, due to insufficient resolution, the experimental X-ray emission spectrum does not always allow to accurately determine contributions of each component to the total density of states. Therefore, for the first time we have used the LMTO method to calculate the total and partial electron energy densities of the constituent elements in ScFe$_2$Si$_2$. Based on these calculations, X-ray emission bands have been evaluated separately from each non-equivalent position of iron and silicon atoms.

Fig. 2 presents in unified energy scale X-ray emission spectra (bottom panel) and K-spectra (top panel) of both silicon and iron. SiL- spectra mainly reflect distribution of *s*-states. Band A in SiL-emission energetically coincides with main band K in FeL-emission that point out at strong hybridization between iron d-states and silicon s-states in the energy range between 0 and 5eV.The degree of hybridization substantially depends on the nearest neighbors of silicon. The calculated intensity of X-ray emission from Si2 (Fig. 3) appears to be lower than that of Si1. It is consistent with analysis of the crystalline structure which shows that the atomic Fe1-Si distances are significantly less as compared with the ones in the polyhedrons containing Fe2 (Table 2).

A similar trend is observed for the Si emission spectra in the 6-11 eV energy range which reflects covalent Si-Si bonds. Indeed, according to Table 2, Si2-Si2 distance (0,2509 nm) is much shorter than Si1-Si1 (0,2891 nm) that correlates well with the calculated emission intensities from Si1and Si2 (Fig. 3).

Fig. 4 shows the experimental and theoretically calculated FeKβ$_{2.5}$-bands, which according to the selection rules reflect density distribution of valence band filled p-states. On the whole, a nearly total coincidence is observed for maxima positions in all

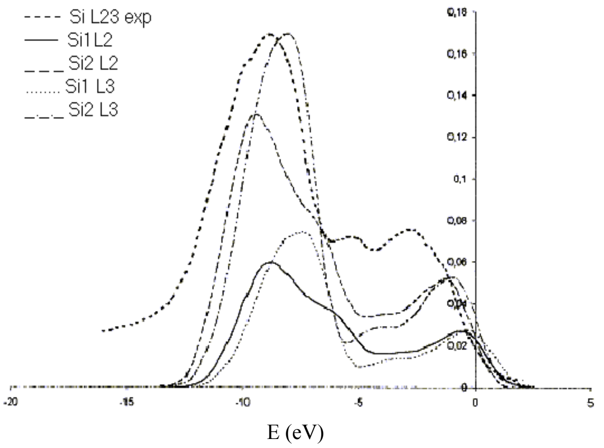


Fig. 3 Calculated and experimental (----) X-ray emission Si L$_{2,3}$ -bands in ScFe$_2$Si$_2$.

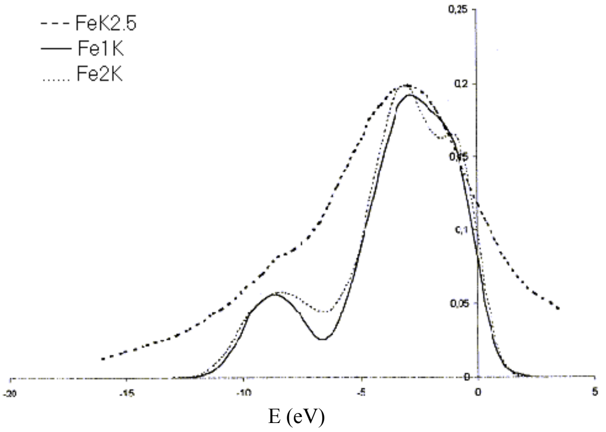


Fig. 4 Calculated (–, ····) and experimental (----) X-ray emission FeKβ$_{2.5}$-bands in ScFe$_2$Si$_2$.

three curves and, at the same time, one should single out the anomalous Kβ$_{2.5}$-band splitting of the Fe2 band. Due to considerable diffusivity of the p-wave functions of iron, the width of experimental band at half of its maximum intensity is larger than the width of the theoretical curves.

The X-ray emission L-band of transition elements allows obtaining information about distribution of *d*-symmetry electrons (Fig. 5). As it can be concluded from Table 3, the main contribution to the calculated intensity of L$_{\text{II,III}}$-band of iron in two crystallographically non-equivalent positions is indeed from electron states of d-symmetry.

The ratio of contributions from the $d_{3/2}$- and $d_{5/2}$-states to the intensity of emission band is considered to be one of the most important characteristics of spin -orbital interaction in the valence band. Without taking into account the spin-orbital interaction, the ratio of these contributions would be:

$$Id_{5/2}/Id_{3/2} = 9 \qquad (1)$$

As it can be seen from Table 3, this calculated ratio for the L$_{\text{III}}$-valence band for the compound with scandium does not differ considerably from the above mentioned number. In our opinion, this can serve as a sufficient reason not to consider the spin-orbital interaction.

The effective numbers of valence electrons of different symmetries per atom n_χ can be estimated from the partial density of electron states as follows:

$$N_\chi = \int_{E_0}^{E_f} N_\chi(E)dE \qquad (2)$$

where $N_\chi(E)$ is the partial DOS which corresponds to relativistic quantum number χ; E_0 is the energy of the valence band bottom; E_F is the energy of the Fermi level.

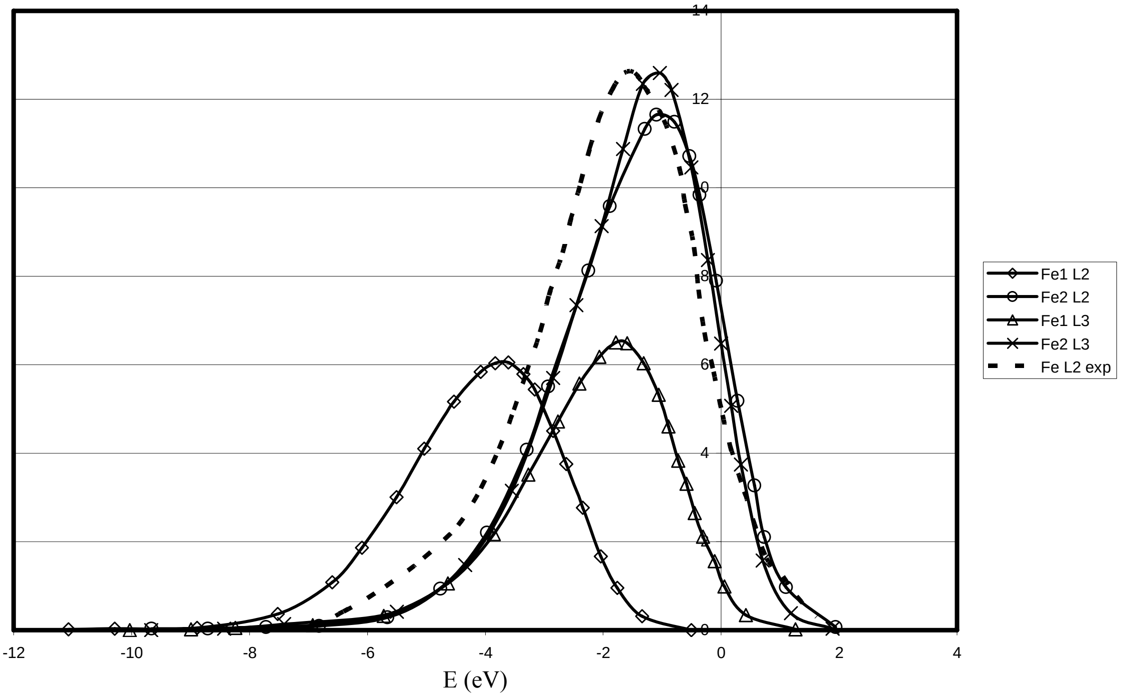


Fig. 5 Calculated and experimental (----) X-ray emission FeL$_{\text{II,III}}$- bands in ScFe$_2$Si$_2$.

Table 3 Calculated contributions of different electronic states to the intensity of X-ray emission bands of $ScFe_2Si_2$ (in %).

Component	K – band		L_{II} – band		L_{III} – band		
	$p_{1/2}$	$p_{3/2}$	$s_{1/2}$	$d_{3/2}$	$s_{1/2}$	$d_{3/2}$	$d_{5/2}$
Sc	32,46	67,54	5,17	94,83	5,35	9,54	85,11
Fe1	32,16	67,84	0,42	99,58	0,45	10,16	89,39
Fe2	32,18	67,82	0,45	99,55	0,48	10,17	89,36
Si1	33,18	66,82	76,13	23,87	80,27	3,02	16,71
Si2	33,26	66,74	80,32	19,68	81,36	2,07	16,57

Table 4 Effective filling numbers of electrons of different symmetries in valence band of $ScFe_2Si_2$.

Component	s	p	d
Sc	0,71366	1,32179	2,53627
Fe1	0,64245	0,94694	6,93994
Fe2	0,53453	0,74734	6,79293
Si1	1,10911	1,64719	0,31026
Si2	0,98860	1,40310	0,20540

Table 5 Mossbauer parameters ^{57}Fe spectrum in $ScFe_2Si_2$ compound.

Mossbauer parameters	1	2	3
Isomer shift (mmsec^{-1})	0,30	0,45	0,30
Quadruple splitting (mmsec^{-1})	0,50	0,20	0,62
Relative line intensity $S_{rel.}$	0,312+0,090	0,516	0,172
$H_{eff.}$ (кOe)	-	140	169

The results of such evaluation of the numbers for the $ScFe_2Si_2$ compound are shown in Table 4.

Analysis of the calculation results show that the degree of occupation of *spd*-valence orbital varies and considerably differs from the number of external electrons in isolated atoms. The occupancy of *d*-orbital of Sc in the $ScFe_2Si_2$ compound is shown to be significantly larger than that in an isolated state. The most interesting, in our opinion, is the analysis of the change of external valence *sp*-states occupation, because it gives us possibility to estimate a contribution of electrons of Si to the chemical bond of the $ScFe_2Si_2$ compound. The electron configuration of Si in the compound can be described as $s^{1.1}p^{1.6}$ (Table 4), which significantly differs from s^2p^2 (atomic Si). Thus, we can state that in the investigated compound, Si atom contributes to the chemical bond with 0,9 electrons of *s*-symmetry per atom (for comparison, Si atom contributes 0,7-electrons per atom in YM_2Si_2 compounds [4]). A similar situation was also observed in case of YM_2P_2 compounds [8, 10]. It is important to note that contribution of the *s*-symmetry electrons to

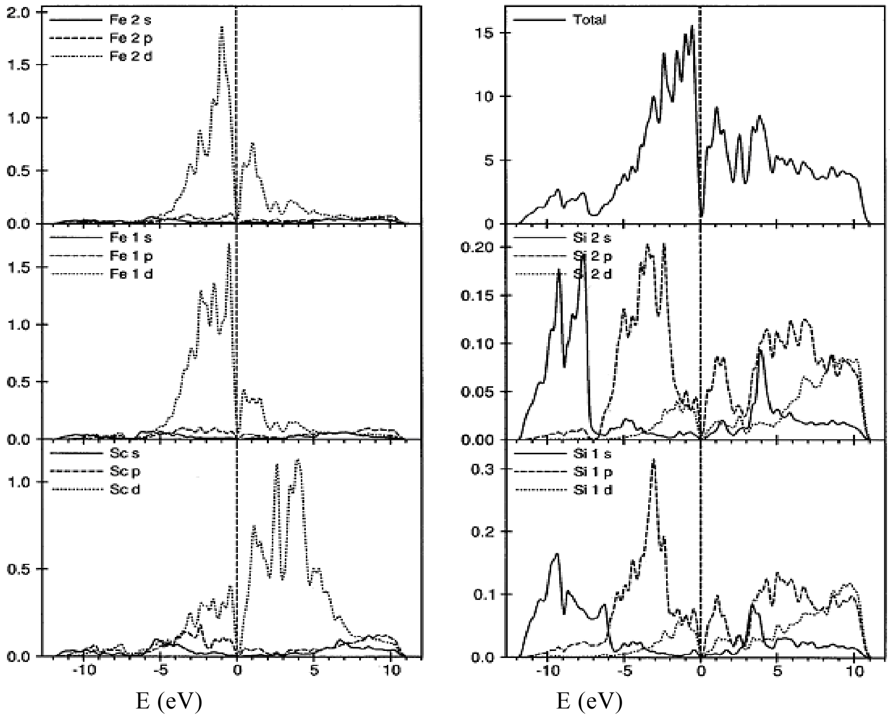


Fig. 6 Total and partial densities of the electron states in $ScFe_2Si_2$ compound.

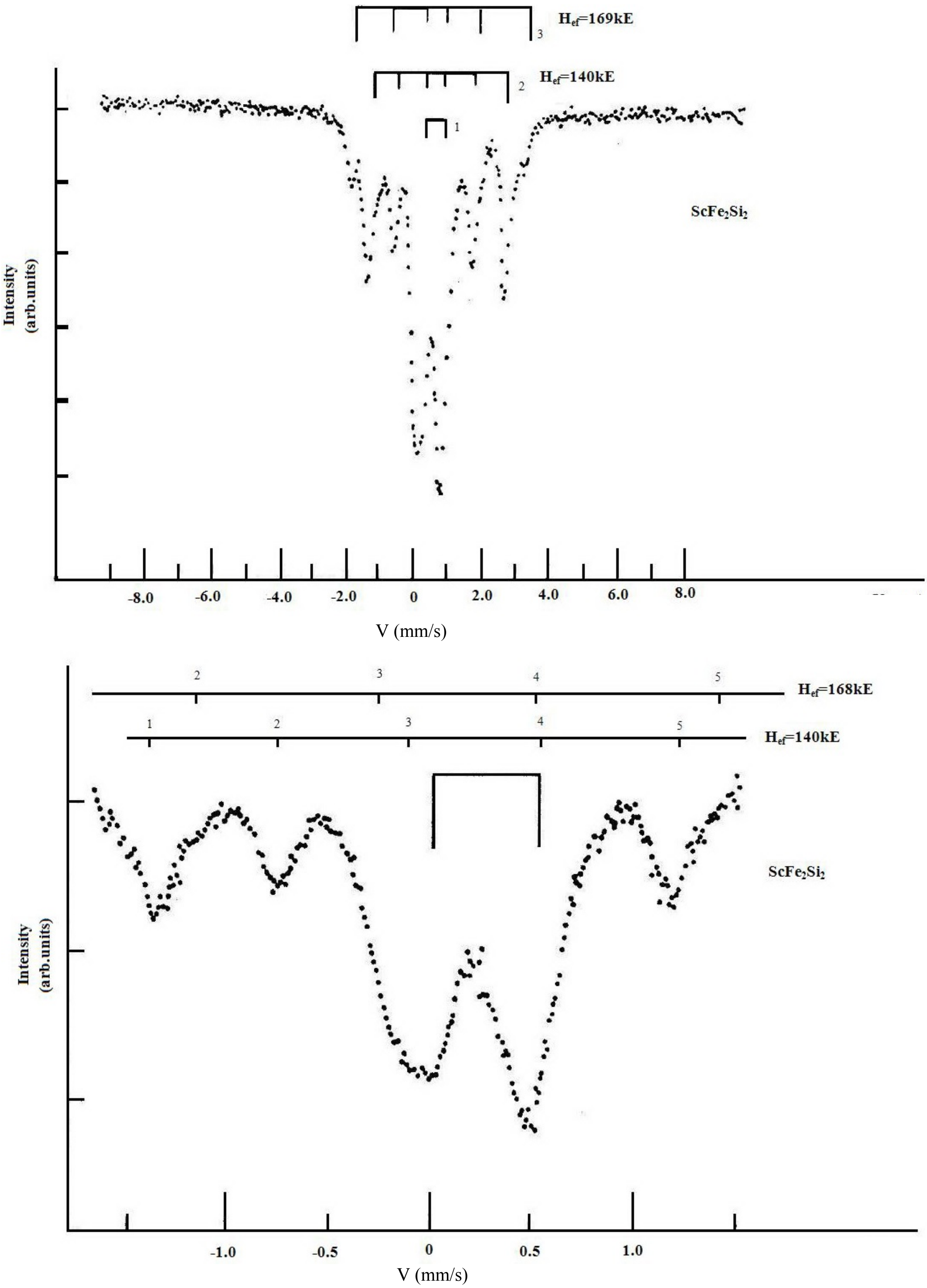
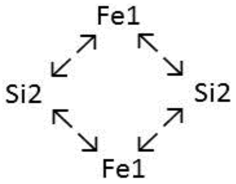


Fig. 7 Mossbauer absorption spectrum for the $ScFe_2Si_2$ compound (T = 298 K).

the chemical bond is substantially different for Si1 and Si2. of non-equivalent iron sites in the crystal structure can often be revealed by the Mossbauer spectrum via so called magnetic or hyperfine splitting. Indeed, as Fig.7 illustrates, the room temperature Mossbauer absorption spectrum for the $ScFe_2Si_2$ compound show a pattern consisting of two overlapping six-line hyperfine splitting structures (2 and 3) as well as one non-magnetic doublet (1).

Mossbauer parameters such as isomer shift, intrinsic magnetic field H_{eff}, quadruple splitting and the relative intensity of absorption lines for each of the spectrum components are presented in Table 5. These parameters significantly differ from the ones reported for $Sc_2Fe_2Si_5$ and $ScFeSi_2$intermetallic compounds [11].

As it follows from Fig. 1 and Table 2, Fe atoms can occupy two non-equivalent crystallographic positions. The polyhedrons of the Fe atoms have the same quantitative and qualitative compositions, however, at the same time, they differ in shape. Fe2 atoms create chains along z-axes where Fe-Fe distance is as short as 2.509 Å known for pure α-Fe. Fe1 atoms, on the other hand, are in contact only indirectly via Si2 atoms, so entire structure looks like a chain of rectangles along y-axes:



As it is seen from the analysis of the crystal lattice, the interpretation of the Mossbauer experimental data cannot be univocal. The amount of crystal lattice sites occupied by the iron atoms is not reflected by the corresponding number of the spectra features.

The paramagnetic spectra component consists of a doublet that reflects iron atoms at the 4(d) crystal lattice position. Significant value of the quadruple splitting (50 $mmsec^{-1}$) points out at strong electrical field anisotropy caused by the nearest neighbors of the Fe1 atoms. Isomeric shift has a positive value which indicates increase of the d- electron and decrease of s-electrons density as compared to atoms in pure iron lattice.

The Fe2 atoms are manifested by component 2 in the spectra with a corresponding intrinsic magnetic field $H_{eff.}$ = 140 кOe. It should be noted that, as seen from Table 4, the quadruple splitting for component 2 is the smallest not only in the studied compound, but, also among other Sc-Fe-Si intermetallics such as $Sc_2Fe_2Si_5$ and $ScFeSi_2$ [11] which may indicate relatively small electrical filed gradient near Fe2 iron nucleus.

The appearance of the lower intensity component 3 is still open to interpretation. It can be suggested that a relatively small substitution Fe1↔Si2 in the crystal lattice will cause Fe1-Fe1 interactions that is revealed by this additional component of the Mossbauer spectra.

4. Conclusions

As it can be seen from the performed calculations and experimental data, the *s*-states of Si hybridize with the *p*-states of Sc and Fe and are located at the bottom of valence band. In the middle of the band, the *p*-states of the constituent atoms are localized, whereas near the Fermi level *d*-states of transition element dominate. Contribution of the *s*-symmetry electrons to the chemical bond is substantially different for Si atoms located in non-equivalent crystallographic positions. Results of Mossbauer absorption measurements are presented which indicate that iron atoms might occupy more than two expected non-equivalent crystallographic positions.

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