

X-ray spectroscopic study of structural isotypism in Me_2Si silicides

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Basing on consideration of the shape, width, energy position, and integral intensity of X-ray spectra of all series as well as of photoemission quantum yield, an attempt has been made to explain the isotypism nature for silicides of transition metals belonging to the beginning and end of the 1st large period.

На основании формы, ширины, энергетического положения и интегральной интенсивности рентгеновских спектров всех серий, а также квантового выхода фотоэмиссии сделана попытка объяснить природу изотипизма силицидов переходных металлов начала и конца первого большого периода.

In silicon technologies, it is often necessary to select a specific metal that, within limits of an isostructure, will provide a certain distribution of electrons and valence states over the valence band under formation of suitable bindings between the metal and silicon atoms [1, 2]. The relationship between the structural isotypism and the electron structure is now under intense investigation. As to silicides, the features mentioned were correlated in part with the crystal chemistry ones [3]. Few metal silicides of Me_2Si composition are known. Those are formed by metals belonging to the beginning of the transition metals (TM) 3d row or, in contrast, locking the row. Among three known silicides of that group, Ca_2Si has the cubic structure of PbCl_2 type and melting point of 920°C. Two other silicides, Co_2Si and Ni_2Si , are of the same $\sigma\text{-Ni}_2\text{Si}$ structure type and have the melting points 1220 and 1320°C, respectively [3]. In this work, the X-ray spectroscopy has been used to study (a) emission K series and absorption K edges of free Ca, Co, Ni and the same elements in silicides and (b) the K and L emission spectra and the L edge of silicon quantum yield in the compounds.

The K series of metals and silicon were studied using a standard DRS-2M spectrograph. When taking the K spectra, the sec-

ondary photon method is used that provides an improved signal-to-noise ratio as compared to the electron beam excitation. A sealed BKhV-7 tube with gold anode is used as the secondary photon source. The tube is operated at 30 kV and 70 mA. Silicon is used as the analyzer crystal. The crystal having the (1340) plane as the reflecting one with the plane spacing $d = 1.174 \text{ \AA}$ is used to examine the K spectra of Co, Ni, and the emission K spectra of Si, while that with the (1010) one at the plane spacing $d = 4.246 \text{ \AA}$ is used to obtain the K spectra of Ca.

The SiL_3 quantum yield spectra were obtained using a RSM-500 X-ray spectrometer-monochromator. To expand the spectrum, a diffraction grating with 600 lines per mm was used, the bending radius being 1980 mm. The spectra were taken in the 1st reflection order. The spectrum taking parameters were chosen so that the resolution was not worse than 0.4 eV. The spectra were processed using the procedure proposed in [4].

Literature data [5, 6] concerning the X-ray spectra of the phases mentioned as well as information obtained by us made it possible to consider the electron structure thereof in a sufficient detailed fashion. The emission and absorption spectra for K and L

series for both components of those phases are compared in the Figure. To analyze the curves, it is possible to adopt, in accordance with the existing concepts of X-ray spectrum information density, that the $K_{\beta_5\beta''}$ emission band of TM represents mainly the d -like $4p$ states of the metal with addition of $3s$ states of Si ($K_{\beta''}$); the K edge of TM absorption represents the distribution of free d -like and $4p$ states within the conduction band and continuum of the np states of the crystal; $K_{\beta_x}-L_{\alpha_{1,2}}$ emission bands of silicon represent the occupied Si p and s states, respectively; the photoemission quantum yield curve (PEQYC) in the region of Si L edge reflects the distribution of the free s states of Si within the conduction band.

It follows from the crystal chemistry data that Si atoms in Me_2Si do not form continuous chains or networks but are bound in pairs (links). Thus, the electron density of the spectrum regions representing the Si-Si bonds must be rather low. As is evidenced by numerous works cited in [7], this is the lowest energy region of the valence band answering to the long-wavelength tails of all emission bands. In fact, the tail regions of $Me K_{\beta_5}$ and Si K_{β_x} emission bands (see Figure) answer to a feature that is interpreted in K_{β_5} bands as the "cross" transition [8] from the non-metal ns level to the $1s$ one of the TM under partial capturing of its $4p$ states ($K_{\beta''}$ satellite). This subband is at a distance of 6 to 7 eV from the main one, it increases in intensity as the Si content rises and the structure elements consisting of Si atoms become stronger, that is, the subband represents the Si-Si bonds. These bonds cannot be provided by the s electrons (spherically symmetric) and require an addition of p states in a part of the band (Si K_{β_x} band) in silicides. In the Figure, there are no appreciable density of $3p$ states in the Si atom sphere for all the Me_2Si while the $3s$ state density is high.

It can be supposed also that in Ca_2Si , d states are "still" not excited by chemical binding while being "already" not excited thereby in Co_2Si and Ni_2Si , since their most rigid component, $d_{\gamma}^2(l_g)$, is lowered and atomized up to the period end while the residual one, $d_{\epsilon}^3(t_{2q})$, is known to be almost unable to be involved into local bindings. This explanation, however, is suitable when the directional bonds in Me_2Si are hybridized according to the dsp type and not to the sp one.

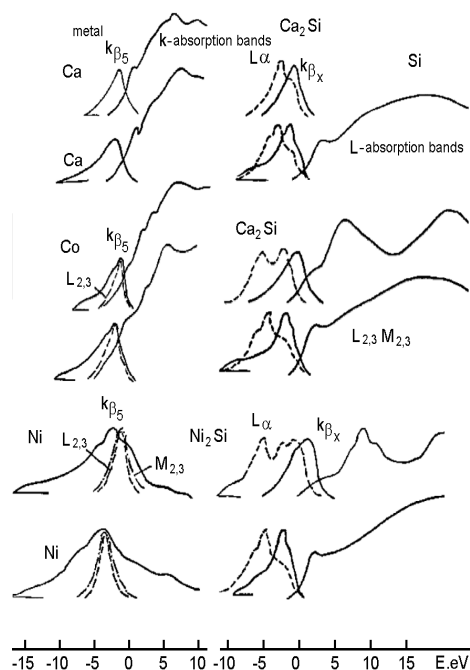


Fig. X-ray emission and absorption bands of the elements Ca, Co, Ni, Si and of the alloys Me_2Si ($Me = Ca, Co, Ni$).

The latter case is most probable for $CaSi$ that is less stable than others [9]. The thin structure of metallic Ca is more simple than that of the next $3d$ metals and is similar to the Si band structure form. The simple dispersion shape of the Ca K_{β_1} emission band is due to that only one low density band is occupied in metallic Ca at the homogeneous distribution of the density over the width. The central parts of valence band in all the Me_2Si are formed by the overlap region of K , L , and M emission band contours, as is shown in the Figure. Those represent the Me-Si bonds and are similar to each other not only in a high hybridization extent (of no doubt dsp type), as is evidenced by the large overlap of those bands, but also in the high state density therein. The both characteristics are more pronounced in the metal atom sphere. As to the Si atom sphere, the local bond band shows one hump (maximum) for Ca_2Si , two for Co_2Si and three for Ni_2Si ; perhaps this is due to crystal structure complication (from cubic to rhombic one) and thus to increase in heterodysmicity of Me-Si bonds in configuration polyhedrons of the nearest environment of the emitting atom.

Perhaps the main distinction in the energy spectrum structure of Me_2Si is the position and shape of the Si K_{β_x} emission band. In Ca_2Si , it is completely symmetric and different enough from pure Si K_{β_x}

band. Almost the same symmetry (with somewhat broadened peak and distorted tail shape) is observed for the isotypic Co_2Si . In both cases, the fact can be explained by a limited penetration of the metal d states into the Si atom sphere for the reason mentioned above (sp hybridization type instead of dsp one).

Maybe the involvement of d electrons in the sp hybridization is a necessary precondition for the multiple-band energy structure of the p subband in the Si atom sphere; this is confirmed by spectra of numerous silicide phases [7]. Consideration of Si spectra reveals another interesting regularity in the Me_2Si electron structure. The Si $K_{\beta x}$ band is always displaced in energy beyond the bounds of Si $L_{\alpha 1,2}$ by 2 to 2.5 eV and only one of silicon bands is crossed by the Fermi surface. Thus, it is formed, from the Si atom side, mainly by three atoms thereof (without $3s$ addition). For that reason, the excitation of $3d$ electrons of Si chemical bond is unlike. That fact explains the metallic character and electrophysical properties of Me_2Si , in particular [7], the narrow high-density band presence near EF (taking into account that the $3d$ and $4p$ states of TM are in the Fermi surface).

If we assume that the split $K_{\beta x}$ band apex is due to degeneration of the metal atom d levels, then in this case, two subgroups of the states are formed (collective $(p_\alpha + d_\gamma)$ and local-binding $(p_\alpha + d_\gamma)_\alpha$ ones) with different chemical bond functions. Due to lowering and atomization of the d_γ component in Co and Ni atoms, it is just the $(p_\alpha + d_\gamma)_\pi$ subgroup of levels that is mainly available for the bond formation in Me_2Si . In consistence with the symmetry properties, this subgroup is poorly superposable with valence sp orbitals of Si. A similar situation takes place only in Ca_2Si where the d_γ component is absent for other reasons (it is difficult to excite by chemical bond). Perhaps this fact might explain the similarity between thermodynamic properties of all the Me_2Si [8] as well as the fact that the TM from middle part of the period (from Ti through Fe) do not form Me_2Si .

Consideration of Ca and Co absorption spectra in Me_2Si evidences the presence of d type vacancies and an appreciable complication of the conduction band structures when passing from Ca_2Si to Co_2Si . Other parameters of those edges are similar to each other (slope, the position and width of the absorption initial region and main maximum). A rather important data on the nearest envi-

ronment character of absorbing Si atom is provided by comparison of the PEQY curves. When passing from pure Si with tetrahedral sp_3 coordination of diamond lattice to more complex rhombic structure of Co_2Si , the PEQY curve is changed substantially: only the initial absorption region remains substantially unchanged, while the curve becomes double-humped. Transition to the isotypic Ni_2Si preserves in general the double-humped PEQY curve shape as well as the energy position of both those absorption maxima in the Si $3s$ state, although some secondary absorption fluctuations appear in the curve. In principle, such a curve shape must be typical of the isotypic Ca_2Si .

Thus, the thin structure of K and L X-ray emission and absorption spectra for isotypic Me_2Si silicides has been studied comprehensively under unique experimental conditions. The relative position of K and L emission bands for $3d$ metals shows a high density of occupied states near the Fermi boundary and a low polarization extent of Me–Si bonds at approximately the same widths of the band regions revealed in the metal and silicon atomic spheres. In the Si atom sphere, the high-energy region is formed by p states while in the transition metal atom one, by p and d states; the low-energy band region in both atomic spheres is formed by s states. For Me_2Si type silicides, it is just the high energy band formed by the d_τ -like wave functions of the metal and p_π ones of silicon that is responsible for the Me–Me binding. The intermediate energy band formed by d_z -like wave functions of the metal and p_σ ones of silicon is responsible for directional local Me–Si bindings of covalent or semi-covalent type. The low energy band is formed mainly by s wave functions of Si with addition of the metal and silicon p functions that provide mainly the Si–Si bonds. Consideration of emission line energy variations and the absorption edges has shown that the charge transfer occurs towards the metal atoms, thus evidencing the accumulation of excess small charge on the metal atoms and agreeing well with the small electronegativity difference between the metals and silicon.

References

1. V.P.Voronkov, V.I.Gaman, M.O.Duchenko, V.M.Kalygina, *Poverkhnost'*, No.2, 35 (1995).
2. O.I.Bomk, L.G. Il'chenko, V.V. Il'chenko, *Sensors and actuators*, B, 131 (2000).
3. E.A.Zhurakovsky, P.V.Gel', *Dokl. AN UkrSSR Ser. B*, No.10, 914 (1977).

4. V.V.Nemoshkalenko, L.I.Nikolaev, A.V.Yushchenko, Preprint, Inst. for Metal Phys., No.3, 87 (1987) [in Russian].
5. E.A.Zhurakovsky, I.N.Frantsevich, X-Ray Spectra and Structure of Silicides and Germanides, Naukova Dumka, Kiev (1981) [in Russian].
6. V.I.Minin, L.D.Finkelshtein, V.G.Zyryakov, S.A.Nemnonov, in: Chemical Bond in Semiconductor and Semi-Metal Crystals, Nauka i Tekhnika, Minsk (1973), p.95 [in Russian].
7. E.A.Gladyshevsky, Crystal Chemistry of Silicides and Germanides, Metallurgia, Moscow (1971) [in Russian].
8. M.A.Blokhin, Physics of X-Rays, Gostekhizdat, Moscow (1957) [in Russian].
9. K.M.Kolebova, S.A.Nemnonov, F.A.Sidorenko, *Fiz.Metal.Metalloved.*, **30**, 309 (1970).

Рентгеноспектральне дослідження структурного ізотипізму у силіцидах Me_2Si

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На основі аналізу форми, ширини, енергетичного положення та інтегральної інтенсивності рентгенівських спектрів усіх серій, а також квантового виходу фотоемісії зроблено спробу пояснити природу ізотипізму силіцидів перехідних металів початку і кінця першого великого періоду.