

## Correlation between chemical shift of Si $K\alpha$ lines and the effective charge on the Si atom and its application in the Fe-Si binary system

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High-resolution Si  $K\alpha_{1,2}$  ( $K-L_{3,2}$ ) x-ray fluorescence spectra of Si, SiB<sub>6</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, and Na<sub>2</sub>SiF<sub>6</sub> were measured on a double-crystal spectrometer. From SiB<sub>6</sub> to Na<sub>2</sub>SiF<sub>6</sub>, the chemical shifts for the Si  $K\alpha$  lines relative to pure Si were 0.05, 0.19, 0.45, 0.62, and 0.96 eV, respectively. The value increased systematically with increased atomic number of the neighbor atoms of Si. Calculation by the discrete variational Hartree-Fock-Slater method showed that the effective charges on Si in SiC and Na<sub>2</sub>SiF<sub>6</sub> were 0.37 and 1.85 electrons, and the values in Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub> were found in former literature to be 1.24 and 1.40 electrons, which increased in the same sequence as the chemical shift. These facts certified the direct correlation between the effective charges on Si and the chemical shift of Si  $K\alpha$  lines. An empirical curve of effective charges on Si versus chemical shifts in Si  $K\alpha$  lines was obtained. With this empirical curve, we found that Si held positive charge in the Fe-Si binary system based on the Si  $K\alpha$  chemical shift measurement, although the electronegativity of Si (1.90) was greater than that of Fe (1.83), which made it seem reasonable to assume that the charge transfer should be from Fe to Si. We determined the effective charges on Si in FeSi<sub>2</sub>, FeSi, and Si steel to be 0.50, 0.56, and 0.63 electrons, which increased with the increasing Fe concentration.

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### I. INTRODUCTION

Chemical-state analysis based on a chemical shift in x-ray fluorescence lines is one of the most important applications of high-resolution x-ray fluorescence spectroscopy. Gohshi *et al.*<sup>1-3</sup> used the chemical shift to determine the chemical state of S, Cr, and Sn in unknown materials. They obtained not only qualitative, but also quantitative results. Kawai *et al.*<sup>4</sup> studied the many-electron effect on the shape and chemical shift of Cl  $K\alpha$  x-ray emission lines. Liu *et al.*<sup>5</sup> measured the high-resolution Pd  $L\alpha$  fluorescence spectra and discussed the possible reason for the relatively small chemical shifts of Pd. The chemical shift of x-ray fluorescence lines is usually interpreted by the effective charges of the x-ray emitting atom.<sup>6,7</sup> For example, the Al  $K\alpha$  lines are shifted to higher energy in going from the metal to the oxide.<sup>8</sup> To know exactly the charge distribution between two atoms is essential in studying the nature of the chemical bonding between these two atoms. In this aspect, chemical shift measurement in x-ray fluorescence spectra has been proved to be a promising method. Many studies on the coordination analysis of Al atoms in oxide compounds using the shifts of Al  $K\alpha$  lines have been reported.<sup>9-12</sup> By comparing the chemical shift and effective charges of the elements studied to those of reference samples, we may determine the chemical state of the atoms in unknown compounds.

The Si  $K\alpha$  x-ray fluorescence spectra have been studied in many previous investigations. Baun and Fischer<sup>13</sup> were the first to use a flow proportional counter instead of photographic recording as detector, and this made it more practicable to perform an analysis concerning the intensity of the spectrum. But as the resolution of their spectrometer was not high enough, there were some errors in the chemical shift of Si  $K\alpha$  lines they reported. Later Demekhin and Sachenko<sup>14</sup>

studied the  $K\alpha$  satellites of Si using a double-crystal spectrometer and electron excitation. Utraiainen *et al.*<sup>15</sup> used a plane crystal spectrometer and fluorescence excitation. Graeffe *et al.*<sup>16,17</sup> measured the Si  $K\alpha$  spectra from Si, SiC, SiO<sub>2</sub>, and Si<sub>3</sub>N<sub>4</sub> on a double-crystal spectrometer. They also used a curved-crystal spectrometer for comparison.

Recently, iron silicides have been extensively studied because  $\beta$ -FeSi<sub>2</sub> could be used as a constituent of Si-based optoelectronic devices since it had a band gap of 0.85 eV.<sup>18,19</sup> Leong *et al.* reported a Si/FeSi<sub>2</sub> multilayer diode that emitted light at a wavelength of 1.5  $\mu$ m, which was suitable to be used in optical fiber communications.<sup>20</sup> Among the numerous theoretical and experimental investigations of iron silicides, the electronic structure of both bulk and epitaxially grown silicides have been performed.<sup>21-24</sup> Ederer and co-workers<sup>25,26</sup> studied the Si  $L\alpha$  lines in both the bulk and multilayer Fe silicides with soft x-ray fluorescence spectroscopy. Hoszowska *et al.*<sup>27</sup> studied the influence of the chemical environment on the Si  $KL$  x-ray satellite spectra of several 3d, 4d and 5d transition-metal silicides, including FeSi<sub>2</sub>. They argued that the Si  $L$ -shell rearrangement probability reflected the bonding properties of transition-metal silicides. However, there is still much debate concerning the chemical state of Fe or Si in Fe silicides and the experimental data are relatively rare compared to theoretical calculation.

In the present study, we measured the Si  $K\alpha$  x-ray fluorescence spectra of some Si compounds and calculated the effective charges on Si in these compounds. By discussing the relation between these two parameters we obtained an empirical curve describing the correlation between the effective charges on Si and the chemical shifts in Si  $K\alpha$  lines. As an application of the present rule, we measured the Si  $K\alpha$

lines in FeSi<sub>2</sub>, FeSi, and Si steel and then determined the effective charges on Si in these materials.

## II. EXPERIMENT

The Si  $K\alpha$  x-ray fluorescence spectra were measured on a high-resolution double-crystal vacuum x-ray fluorescence spectrometer (Rigaku, Japan), with two ADP (ammonium dihydrogen phosphate: NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>,  $2d=1.0640$  nm) as analyzing crystals. We measured every spectrum twice using Cr and W anode x-ray tubes as an excitation source, respectively. The line shapes in these two measurements were similar, which showed the satisfactory reproducibility of this spectrometer; only the intensity was greater when the Cr x-ray tube was used. Here we presented the spectra obtained with the Cr x-ray tube. Both Cr and W anode x-ray tube excitation sources were operated at 30 kV and 30 mA. Details of the instrumental setup have been described before.<sup>28</sup> The resolving power ( $5 \times 10^{-4}$  deg in  $2\theta$ ) and the reproducibility (better than 0.4 s in arc) of the instrument were very satisfying. Powdered specimens (SiB<sub>6</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, Na<sub>2</sub>SiF<sub>6</sub>, FeSi, and FeSi<sub>2</sub>) were pressed into briquettes; Si and Si steel (Fe-3 wt % Si alloy) were solid slices and used as received. The samples were then mounted onto sample holders before introduced into the vacuum chamber, which was of  $3 \times 10^{-1}$  Torr. The spectra were recorded in a stepwise mode (with a step of  $0.0005^\circ$  in  $2\theta$  — i.e., 0.01 eV at 1740 eV). The average counting rate at the peak maxima was 20–40 counts per second, and the dwell time for each data point was thus adjusted so that the intensities of all the samples at peak maxima were nearly the same. Before and after each experiment, we measured the spectra of pure Si and applied the peak position of the Si  $K\alpha_1$  line in the pure Si wafer at 1739.98 eV from Bearden's table<sup>29</sup> to calibrate the instrument. The spectra were plotted in energy scale.

## III. RESULTS AND DISCUSSION

The Si  $K\alpha$  spectral profiles of Si, SiB<sub>6</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, and Na<sub>2</sub>SiF<sub>6</sub> are shown in Fig. 1 after normalization with respect to the peak maximum. The measured spectra were at first numerically smoothed 5 times by a least-squares method of Savitzky and Golay<sup>30–32</sup> (second order, seven points). The Si  $K\alpha_1$  and  $K\alpha_2$  peaks were partly resolved, but as we would like to concentrate on the chemical shifts of Si  $K\alpha$  lines, we did not try to resolve the individual intensity of  $K\alpha_1$  and  $K\alpha_2$  lines from the overlapped line shape. The chemical shifts were defined as the energy changes in Si  $K\alpha$  doublets, the positions of which were determined at the center energy of full width at 9/10 of  $K\alpha$  peak maxima. In such a way we might avoid errors introduced during the resolving procedure of  $K\alpha_1$  and  $K\alpha_2$ . We chose these samples because the electronegativity of neighbor atoms of Si in these samples increased in the order of Si < B < C < N < O < F (Si: 1.90, B: 2.04, C: 2.55, N: 3.04, O: 3.44, F: 3.98, defined by Pauling<sup>33,42</sup>). We were interested in the effect of the gradually changed coordination environment on the chemical shift of Si  $K\alpha$  lines. Here we did not

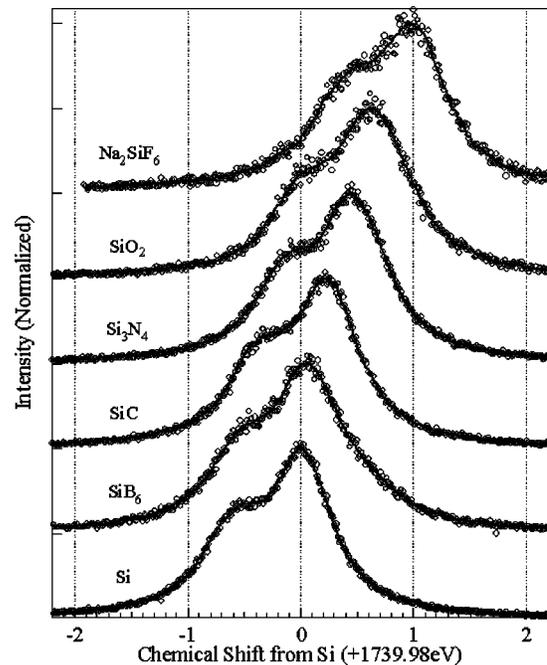


FIG. 1. The Si  $K\alpha$  x-ray fluorescence spectra of Si compounds. Dot: the raw experimental data. Solid line: after Savitzky-Golay smoothing. The parameters of smoothing are given in the text.

take account of the effects of the coordination number of Si in these compounds, as its effect on the chemical state of Si was minor to that of the electronegativity of neighbor atoms. The chemical shifts of Si  $K\alpha$  lines of samples referred to that of pure Si are summarized and listed in Table I. Some results of former studies are also shown.

The chemical shifts were all positive and the value in-

TABLE I. Chemical shifts for Si  $K\alpha$  lines and the effective charges on Si.

Sample	Chemical shifts for Si $K\alpha$ lines <sup>a</sup> (eV)			Effective charges on Si (electrons per Si atom)
	This work	$G^b$	$N^c$	
SiB <sub>6</sub>	0.05			
SiC	0.19	0.23	0.25	0.37
Si <sub>3</sub> N <sub>4</sub>	0.45	0.43	0.49	1.24 <sup>d</sup>
SiO <sub>2</sub>	0.62	0.58	0.60	1.40 <sup>e</sup>
Na <sub>2</sub> SiF <sub>6</sub>	0.96			1.85
Si steel	0.24			0.63
FeSi	0.21			0.56
FeSi <sub>2</sub>	0.19			0.50

<sup>a</sup>With pure Si as reference, the  $K\alpha_1$  peaks of pure Si located at 1739.98 eV. The error for the determination of the peak position was 0.01 eV, so the error of the chemical shift was estimated to be 0.02 eV.

<sup>b</sup>Graeffe *et al.* (Ref. 16).

<sup>c</sup>Nefedov (Ref. 34).

<sup>d</sup>Zhao and Bachlechner (Ref. 38).

<sup>e</sup>Okura *et al.* (Ref. 37).

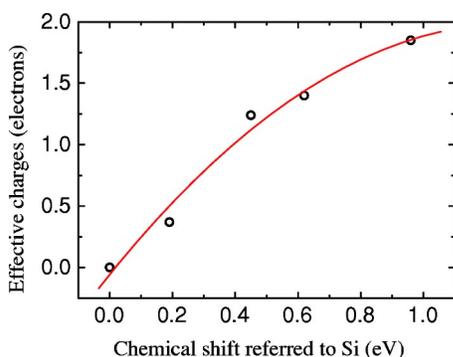


FIG. 2. The correlation between the effective charges on Si and the chemical shift in Si  $K\alpha$  lines.

creased linearly when the neighbor atoms of Si went from B to F, which meant that Si in all these samples held positive charges. There were some differences between the present results and the data reported before. For  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$ , the chemical shifts in the present study were in good agreement with those of Graeffe *et al.*<sup>16</sup> and Nefedov.<sup>34</sup> But the deviation of SiC was a little bit larger, to an extent of 30%. The reason might be that the resolution power of the former x-ray spectrometer was not so satisfying. When the chemical shift decreased, the error became more obvious.

Here we want to pay more attention to the correlation between the effective charges on Si and the chemical shifts of Si  $K\alpha$  lines. The electronegativity of neighbor atoms increases from B to F. It is possible that the effective charges on Si atoms increase as well. We calculated the effective charges on Si atoms in SiC and  $\text{Na}_2\text{SiF}_6$  by the discrete variational (DV) Hartree-Fock-Slater ( $X\alpha$ ) method.<sup>35,36</sup> The number of random sampling points in the DV- $X\alpha$  calculation was 2500. The effective charges on Si in  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  have been calculated by Okura *et al.*<sup>37</sup> and Zhao and Bachlechner,<sup>38</sup> respectively, and we adopted the results from their study. For SiC, we used a  $[\text{SiC}_4]$  tetrahedral model cluster. The bond length of Si-C was 0.189 nm. For  $\text{Na}_2\text{SiF}_6$ , we used a  $[\text{SiF}_6]^{2-}$  octahedral model and the bond length of Si-F was 0.168 nm. It was reasonable to assume that in pure Si the effective charge was zero. For  $\text{SiO}_2$ , the authors<sup>37</sup> used a tetrahedral of  $[\text{SiO}_4]$ .  $\text{Si}_3\text{N}_4$  had a hexagonal structure, and the authors<sup>38</sup> used a supercell containing 52 atoms in their calculation. All the effective charges data are listed in Table I. The effective charges versus chemical shifts are plotted in Fig. 2.

There is a direct relationship between chemical shift and effective charges. As reported by Petrovich *et al.*<sup>39</sup> a smaller effective number of electrons in the valence band shifts the inner-shell electrons to higher binding energy, resulting in a higher energy for the  $K\alpha$  emission line. When the effective charges increased, that the  $K\alpha_{1,2}$  line ( $K-L_{3,2}$ ) shifted to higher energy, so it seemed that the deep shift in the  $K$  shell was larger than that of the  $L$  shell. The electronegativity of neighbor atoms affected the chemical shifts via changing the effective charges on Si atoms.

In Fig. 2, a second-order polynomial fitting (shown as a solid line) seemed to best describe the correlation between effective charges and the chemical shift. The tendency was

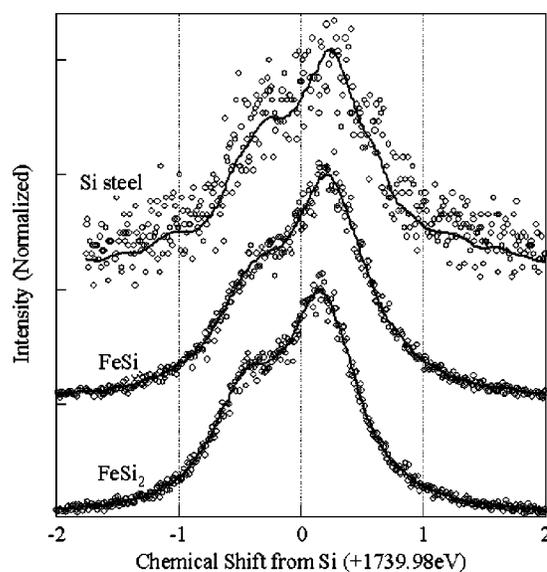


FIG. 3. The Si  $K\alpha$  x-ray fluorescence spectra of Si compounds. Dot: the raw experimental data. Solid line: after Salvitzky-Golay smoothing. The parameters of smoothing are given in the text.

similar to the results of Na, Al, P, S, Cl, and Ar, which were reported by Leonhardt and Meisel.<sup>6</sup> Thus, by calculating the effective charges on Si in some Si compounds with relatively simple structure, we obtained an empirical curve describing the correlation between chemical shifts of Si  $K\alpha$  lines and the effective charges on Si atom. With this curve, we may determine the effective charges on Si in unknown compounds with complicated structure as long as we know the chemical shift of Si  $K\alpha$  lines. Even if we can calculate the effective charges directly for some unknown compounds, this empirical curve can also provide some experimental support or serve as a reference. To apply the present rule, we next measured the Si  $K\alpha$  spectra of  $\text{FeSi}_2$ , FeSi, and Si steel and deduced the effective charges on Si in these materials.

As the electronegativity of Si is larger than that of Fe (1.83), it is natural to assume that in the Fe-Si binary system, Si holds negative charge and Fe holds positive charge. However, from the chemical shift data of our x-ray fluorescence spectra of iron silicides and Si steel, we found that this assumption was not correct, as will be described below.

The measured Si  $K\alpha$  lines of  $\text{FeSi}_2$ , FeSi and Si steel are shown in Fig. 3 and the specific chemical shift data are listed in Table I. The chemical shifts of Si  $K\alpha$  lines in these three samples were all positive, which clearly proved that Si held positive charge. This seemed to suggest that the electronegativity of Fe (1.83) was a little bit lower than estimated or the value of Si (1.90) a little bit higher than estimated. When the concentration of Fe increased in the Fe-Si binary system, the chemical shifts increased as well, indicating more positive charges on Si. From the curve in Fig. 2, we calculated the effective charges on Si atoms in  $\text{FeSi}_2$ , FeSi, and Si steel to be 0.50, 0.56, and 0.63 respectively.

Mäder *et al.*<sup>40</sup> calculated the electron density in metastable FeSi (CsCl type) and  $\text{FeSi}_2$  (CaF<sub>2</sub> type) by an *ab initio* full-potential linearized augmented-plane-wave (FLAPW)

method. They reported that, in FeSi<sub>2</sub>, Si lost 0.13 electron to Fe and, in FeSi, Si lost 0.18 electron to Fe. The values were smaller than the present results, for the samples they studied were not bulk stable Fe silicides. But the results revealed a charge transfer from Si to Fe, which was in good agreement with the present conclusion. Hong *et al.*<sup>41</sup> studied the Si 2*p* core-level binding energy in Fe silicides epitaxially grown on Si(111) and found that compared with pure Si, the Si 2*p* core-level energy shifted to higher energy in Fe silicides, which could be interpreted as arising from electron charge transfer from Si to Fe. Furthermore, they found with increasing Fe concentration, the energy shift of the Si 2*p* level became larger, indicating more charges transferred. This was also consistent with the present study. This comparison was very helpful since it was not easy to obtain high-quality x-ray photoelectron spectra as it was sensitive to surface contamination and needed high vacuum.

Bulk FeSi<sub>2</sub> is a semiconductor with a band gap of 0.85 eV, while the FeSi is a narrow-gap semiconductor (0.05 eV) and the Si steel is metallic. With increasing Fe concentration, the Fe-Si binary system shows less semiconducting properties and gradually turns into metal. From the present study, it seems possible to determine whether the Fe-Si binary system is a semiconductor or a metal by monitoring the effective charges on Si, which can be realized easily by measuring the chemical shifts of Si *Kα* lines. The value of 0.56 seems a critical one. When the effective charge on Si is below 0.56, the Fe-Si binary system is a semiconductor, and when the value is greater than 0.56, it may turn into a metal. As the Fe concentration is the only experimental variable which causes

the above-mentioned results, we may control the properties of the Fe-Si binary system by simply changing the concentration of Fe.

#### IV. CONCLUSIONS

By measuring the chemical shift of Si *Kα* lines and calculating the effective charges on the Si atom, we found that there is a direct relationship between these two parameters. The chemical shift of Si *Kα* lines increased monotonically when the effective charges on Si increased. We obtained an empirical curve which described the correlation between effective charges and the chemical shift in *Kα* lines. By this empirical curve, we found in the Fe-Si binary system that Si held a positive charge though its electronegativity was larger than that of Fe, and the positive charge increased with increasing Fe concentration. The relative electronegativity of Fe (1.83) and Si (1.90) seemed not so exact. It might be feasible to determine the properties of the Fe-Si binary system (semiconductor or metal) by measuring the Si *Kα* fluorescence spectra.

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