Electronic structure and $K$-edge X-ray absorption of iron monosilicide

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Abstract. In this paper, we present theoretical modelling of the band structure of iron monosilicide FeSi. Special attention is paid to the total and partial densities of electronic states along with $K$-edge X-ray absorption near edge spectra of iron. A good agreement was found between known experimental data and our theoretical calculations.

1. Introduction

Recently, great interest has been shown in the experimental and theoretical study of the physical properties of half-metallic ferromagnetic alloys, clusters, multilayer nanostructures, and silicon-based nanofilms [1-4]. The investigation of such systems requires exhaustive knowledge of the physical properties of the structures that are most similar to them in their composition. For example, FeSi studies are needed to investigate an $\text{Co}_2\text{FeSi}$ alloy [5] or multilayer nanostructure $\text{Co}_{45}\text{Fe}_{45}\text{Zr}_{10}/\text{SiO}_2$ [6]. In addition, a very new growth in interest in compounds and nanostructures based on iron and silicon stems from the fact that in recent years silicon nanostructures have found fundamentally new applications in areas far from traditional electronic applications. For example, silicon nanostructures are used in biomedicine and theranostics, when silicon-based nanoparticles are paired with structures of natural origin [7, 8], in particular, with transferrin [9], which carries out the transport of iron ions in the body, and with ferritin [10], which serves as the ubiquitous spherical cage-like iron storage protein in humans and animals. Finally, over the past decades, evidence has emerged that in addition to clathrate crystals [11-13], which are promising thermoelectric materials, many effective thermoelectric materials belong to the class of topological insulators and Weyl semimetals [14-17]. One such material is FeSi. Iron monosilicide is a semiconductor with an indirect band gap at temperatures from 100 K to 200 K. However, outside of this temperature range it behaves like a "bad" metal. Various mechanisms have been proposed to explain this unique electronic and magnetic behavior: electron-phonon interactions, spin fluctuations, and charge excitation [18].

The aim of this work is a theoretical study of the electronic structure of iron monosilicide FeSi. Special attention is paid to the Fe $K$-edge X-ray absorption near edge spectra (XANES).
2. Computational details
The calculations were performed using density functional theory (DFT) as implemented in the Wien2k software package [19] with a full-potential augmented plane wave plus local orbitals (FP-APW+lo) method [20]. The calculation of FeSi was performed by the bulk FP-APW+lo method with the exchange-correlation functional in the modified Becke-Johnson exchange-correlation potential (mBJ-LDA) approximation, which provides a more accurate value of the bandgap width of semiconductors and dielectrics [21].

To calculate the densities of electronic states and band structures of the ground state, an ordinary unit cell and 10000 k-vectors in the first Brillouin zone were used. A supercell and 200 k-vectors in the first Brillouin zone have been employed to calculate the electronic structure of the excited state, which is necessary to correctly describe the XANES spectra. The plane waves were expanded up to the cut-off parameter, \( k_{\text{max}} \), satisfying the relation \( R_{\text{mt}} \times k_{\text{max}} = 7 \), where \( R_{\text{mt}} \) is the radius of the muffin-tin sphere.

At atmospheric pressure, iron monosilicide (naquit) is stable up to a temperature of 1683 K [22]. The naquite (FeSi) belongs to the cubic system with a space group of symmetry \( \text{198}_P\text{213} \) and has a unit cell with parameters \( a = b = c = 4.4860 \) Å, which contains 4 formula units. The coordinates of the atoms in the unit cell are given in table 1 [23].

| Atomic positions | x/a   | y/b   | z/c   |
|------------------|-------|-------|-------|
| Fe               | 0.6340| 0.6340| 0.6340|
| Fe               | 0.8660| 0.3660| 0.1340|
| Fe               | 0.3660| 0.1340| 0.8660|
| Fe               | 0.1340| 0.8660| 0.3660|
| Si               | 0.3445| 0.3445| 0.3445|
| Si               | 0.1555| 0.6555| 0.8445|
| Si               | 0.6555| 0.8445| 0.1555|
| Si               | 0.8445| 0.1555| 0.6555|

To simulate the XANES spectra, a band calculation was performed for the excited state. For this purpose, a core hole is created and one electron is added to the conduction band to maintain electroneutrality. To eliminate the interaction of neighboring excited atoms, a supercell with a volume larger than that of the unit cell is created. The size of the supercell is chosen so that the calculations for two consecutive enlargements of the supercell coincide with each other. To calculate the \( K \)-edge XANES, a core hole was created at the 1s core level according to the \( K \)-edge XANES measurement mechanism where core electrons absorbing a beam of high-energy photons are knocked out from the 1s level. The calculation was carried out by using the universal generalized gradient approximation (PBE-GGA).

3. Results and discussion
Figure 1 shows the structure of FeSi and its first Brillouin zone. The structure was visualized using the XCrySDen software [24].
Figure 1. Elementary cubic primitive cell and the first Brillouin zone of FeSi. The red line indicates the path around the irreducible part of the Brillouin zone when calculating the band structure.

The band structure for the ground state of FeSi is shown in Figure 2. The width of the valence band of FeSi, the minimum of which falls at the point Γ, was 13.12 eV. The valence band has two competing maxima (ceilings): in the Δ direction and the Λ direction. Moreover, the bottom of the conduction band falls in the Σ direction of the first Brillouin zone. The calculated band gap for FeSi is 0.127 eV which is in agreement with the experimental value of 0.13 eV to within hundredths [25].

Figure 2. Band structure of FeSi.
Figure 3 shows the spectra of the total and local partial densities of electronic states (DOS) obtained on the basis of the band calculation for the ground state of FeSi.

![Figure 3. The total and partial DOS of FeSi.](image-url)
Analysis of the partial DOS of FeSi shows that the main contribution stems from the $d$-states of iron, localized in the range from $-6$ eV to the Fermi level. At the same time, the $s$ and $p$ states of silicon are predominantly localized in the ranges $6.5 - 13$ eV and $0 - 7$ eV below the Fermi level, respectively.

The modeling XANES spectrum is very important due to the possibility of comparing the experimental spectrum to the theoretical results. The XANES spectrum reflects the distribution of the density of states that contribute to the formation of the conduction band [26]. We calculated the $K$ absorption spectrum, which was modeled using the universal PBE-GGA functional because it allows us to obtain reliable results for both metals and semiconductors when calculating the XANES spectra [27, 28].

Figure 4 illustrates a comparison of the experimentally measured Fe $K$-edge XANES spectrum (FeSi$_{\text{exp}}$) [29] and the theoretical spectrum (FeSi$_{\text{calc}}$) of FeSi. The absorption edge is found at an energy of $\sim7110$ eV, followed by a local maximum at an energy of $\sim7124$ eV. The main maximum is located at an energy of $\sim7140$ eV. At energies above $\sim7145$ eV the spectra begin to differ since we are dealing with a different scattering mechanism - EXAFS (Extended X-ray Absorption Fine Structure), where the main contribution to absorption arises from a single photoelectron scattering [30, 31].

![Comparison of experimental and theoretical XANES K spectra of iron in FeSi.](image)

**Figure 4.** Comparison of experimental [29] and theoretical XANES $K$ spectra of iron in FeSi.

### 4. Conclusions

A good agreement of our calculations with the experimental data has been demonstrated. The results obtained in this paper can be used to analyze the electronic structure of systems based on silicon and iron.

### Acknowledgments

The study was supported by Russian Science Foundation (Project 19-72-20180) in part of band structure and DOS calculations (SIK).

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