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Structure, Electronic Structure and Properties of Silicides Compound Systems

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The stable lattice constant of silicid compound Mn-Si is calculated theoretically by the first principle calculation and is compared with the experiment. Then electronic structure of Mn-Si is calculated: characters of electronic states such as an atomic origin are discussed. The obtained electronic structure is used to calculate the X-ray emission spectra, whose results agree well with the experiment.

Key words: FLAPW, higher manganese silicides, electronic structure, X-ray emission

1. INTRODUCTION

Metallic silicides such as β-$FeSi_2$, $MnSi_x$ (x=1.67-1.75), and Mg_2Si are attracting much attention in many areas in electronics industry. Study in both basic and applied study is developing in the thermoelectricity, light emission and detection, and photovoltaic effect [1-4].

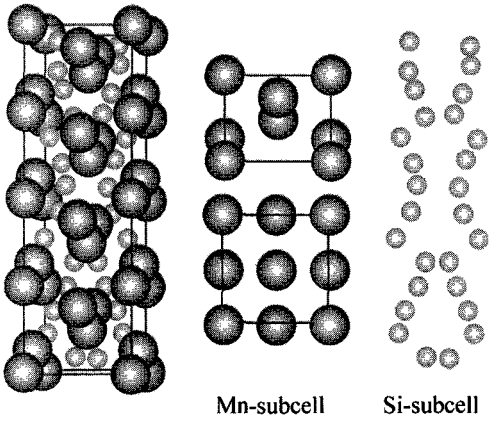
$MnSi_x$ (x=1.67-1.75) is called higher manganese silisides (HMS), which have many polycrystalline type structures such as Mn_4Si_7, $Mn_{11}Si_{19}$, $Mn_{14}Si_{23}$, $Mn_{15}Si_{26}$ $Mn_{26}Si_{45}$ and so on. Most have tetragonal structure while $Mn_{14}Si_{23}$ is orthorhombic. This system has been studied much because of the high potential application as thermoelectric materials at higher temperature. However, due to the complicated crystal structure, detailed studies of electronic properties have been done little [5]. Extensive studies of optical properties have been started recently.

In the present study we pay attention to Mn_4Si_7 and $Mn_{15}Si_{26}$ system, which have simpler structure among HMS and the recent measurement of optical properties enables us to discuss the relation to the detailed electronic structure. By using the first principle electronic structure calculation, the band structure of Mn_4Si_7 and $Mn_{15}Si_{26}$ is calculated.

Here we start from the determination of the lattice constants of Mn_4Si_7 theoretically from the minimization of the total energy. It will be shown that the determined lattice constants are very close to the experimental values. Next the electronic band structure and the detailed density of states will be calculated: discussion on the atomic origin of the various electronic states will be performed. The above results will be used to calculate the X-ray emission spectra of $MnSi_{1.7}$ that Wang *et al.* measured [4]. It will be shown that calculated X-ray emission spectra agrees well with the experiment.

2. METHOD

The Mn_4Si_7 and $Mn_{15}Si_{26}$ have the tetragonal structure and belong to the space group P42c as shown in Fig.1. According to the crystallographic data by O. G. Karpinskii *et al.* lattice constants in Mn_4Si_7 and $Mn_{15}Si_{26}$ are a=5.525 Å, c=17.463 Å and a=5.531 Å, c=65.311 Å, respectively [9]. Firstly, the lattice constants in Mn_4Si_7 are determined theoretically from the minimization of the total energy.



a=0.5525 nm c=1.7463 nm

Fig.1 Crystal structure of Mn_4Si_7

In order to obtain the total energy we need to know the electronic structure, which is calculated from the first principle calculation. The FLAPW method is used based on the density of functional method [10]. The electron density was computed self-consistently by solving a Kohn-Sham equation. The exchange-correlation energy is treated with the generalized gradient approximation by using Predew-Burke-Ernzerhof expression [11]. For silicon and transition elements valence electrons were considered up to d-states and f-states, respectively. In the self-consistent calculation for Mn_4Si_7 k-sampling of the 136 points are taken in an irreducible Brillouin zone (BZ). Radii of muffin-tin (MT) spheres are Mn: 2.0 a.u. and Si: 2.0 a.u..

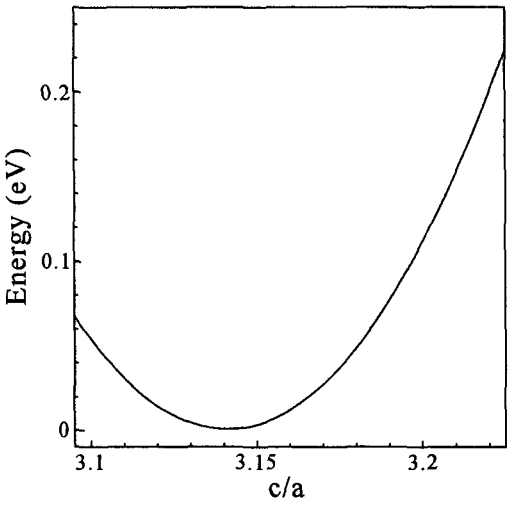


Fig.2 Total energy dependence for the lattice constant ration c/a

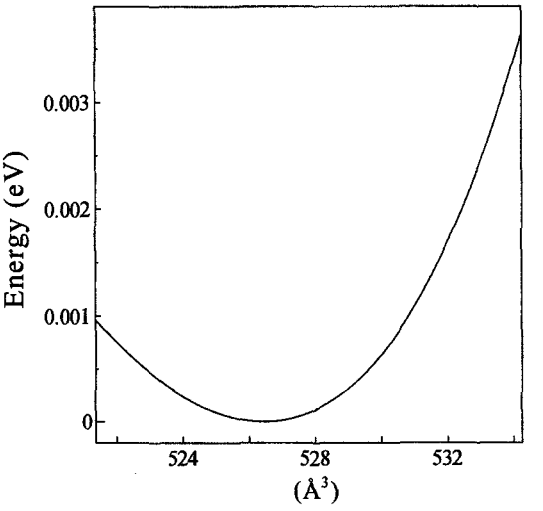


Fig.3 Total energy dependence for the unit cell volume $v=a^2c$

3. STRUCTURE AND ELECTRONIC STRUCTURE

Now let us show the calculated total energy variation for change of the ratio of the lattice constants c/a and the unit cell volume $v=a^2c$, shown in Fig.2 and 3, respectively. Then we find the minimum energy is realized at the value of the lattice constants a=b=5.537 Å c=17.390 Å. The difference between the experimental and theoretical results is smaller than 0.2 %.

The band structure and the density of states (DOS) in Mn_4Si_7 and $Mn_{15}Si_{26}$ are shown Fig.4 and Fig.5, respectively. Dotted lines denote the Fermi energy. In the figure for DOS, the partial densities of states due to Si and Mn are also shown. In Mn_4Si_7 the energy gap is indirect gap of Eg=0.7 eV between Γ (valence band) and X (conduction band). Valence and conduction bands consist of many mixed bands with parabolic-like s, p and flat-like d character.

In $Mn_{15}Si_{26}$ the overall electronic structure resembles with that in Mn_4Si_7. However, the Fermi energy exists at the position, being slightly lower than the top of the valence band. This means the $Mn_{15}Si_{26}$ behaves as heavily doped p-type semiconductor.

It is noted that Imai *et al.* have calculated the electronic structure by the first principle pesudopotential method in many metal silicides, which include Mn_4Si_7 and $Mn_{11}Si_{19}$: only the density of states is shown [5]. The presently calculated density of states in Mn_4Si_7 is in good agreement with their results. Also the result in the $Mn_{15}Si_{26}$ is very similar to that in $Mn_{11}Si_{19}$.

For the purpose of the comparison we have also calculated the electronic structure and the density of states in bulk Si, which are shown in Fig.6. From the comparison of Fig.4 and 5 with Fig.6 we may notice Mn-Si systems have the strong

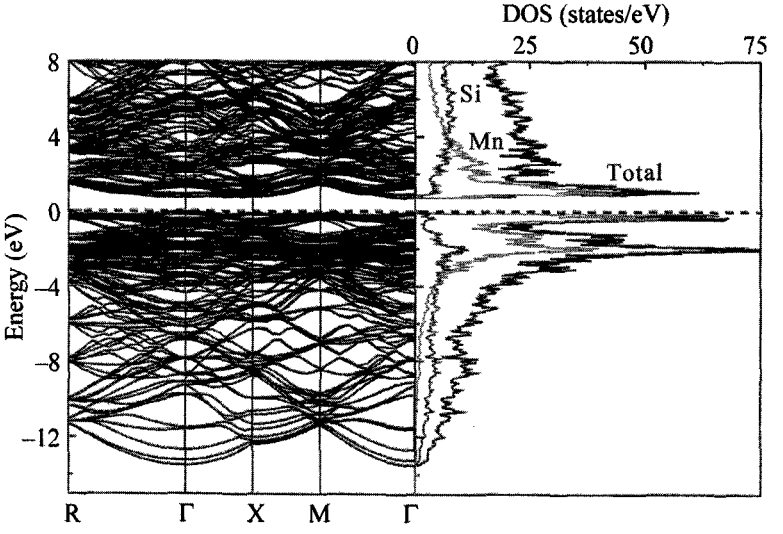


Fig.4 Electronic band structure and DOS for Mn_4Si_7. The energy is referred to the Fermi level. In DOS the partial DOS due to Si and Mn are also shown.

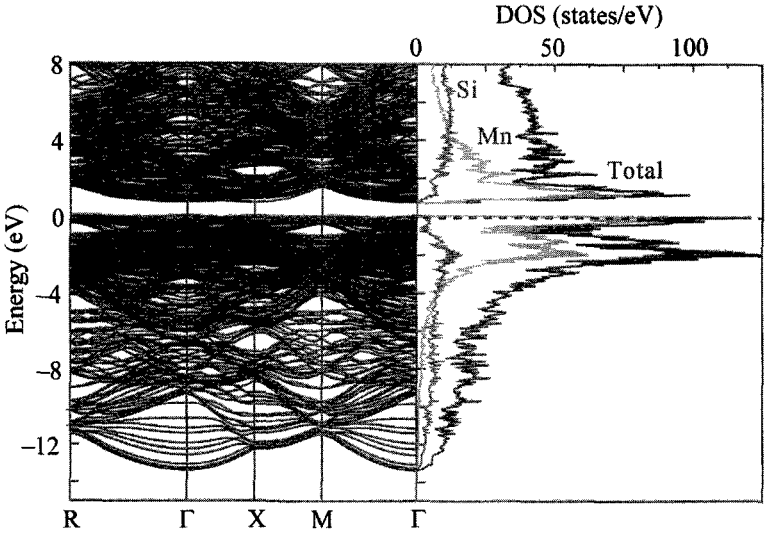


Fig.5 Electronic band structure and DOS for $Mn_{15}Si_{26}$. The energy is referred to the Fermi level. In DOS the partial DOS due to Si and Mn are also shown.

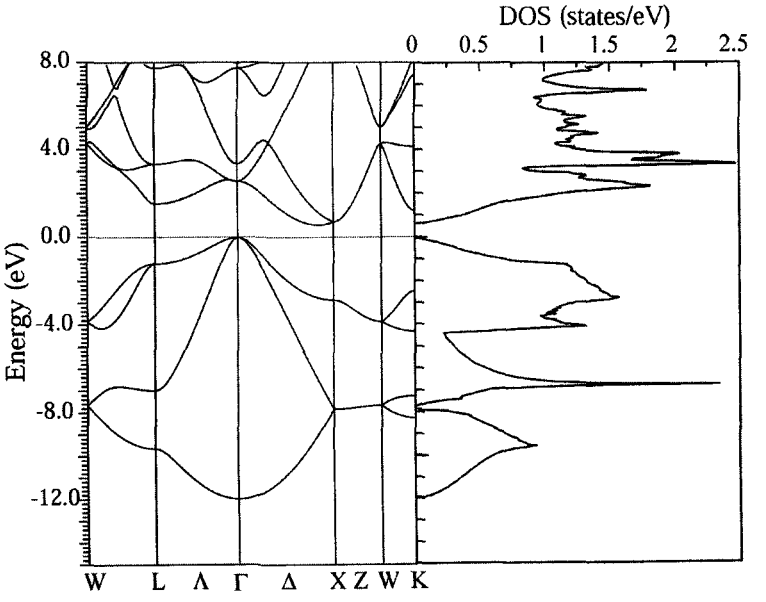


Fig.6 Electronic band structure and DOS for Si. The energy is referred to the respective Fermi level.

d-character flat bands, which yield the sharp DOS at the both conduction and valence band edges.

4.X-RAY EMISSION SPECTRA

X-ray emission spectra at near edge reflect a partial DOS of each atomic orbital for the valence bands. The cross-section of X-ray emission within the dipole approximation is given as

$$\sigma_{emis}(\omega) = 4\pi^2\alpha\omega\sum_{nk}\sum_{imj} N_i \left|\hat{\varepsilon}\cdot\left\langle nk\left|\hat{r}\right|imj\right\rangle\right|^2 \times \delta(\hbar\omega - \varepsilon_{nk} + \varepsilon_{imj}), \quad (1)$$

where ε_{nk} is the energy of a valence electron with the n-th band and the crystal momentum k, and ε_{imj} is the energy of a core state, characterized by the primary index m and the total angular momentum j at the i-atom. Core states are computed by the fully relativistic treatment. N_i is the number of i-atom, α is fine-structure constant. As low-energy core states (K, L, M,) are localized in the muffin-tin (MT) sphere, integral of the $\left\langle nk\left|\hat{r}\right|imj\right\rangle$ is restricted in a MT sphere. The k-sum is carried out by the tetrahedron method.

By using the calculated electronic structure and the wave function, Si $L_{2,3}$ X-ray emission spectra are calculated and are compared with the experimental one. Si $L_{2,3}$ X-ray emission spectra

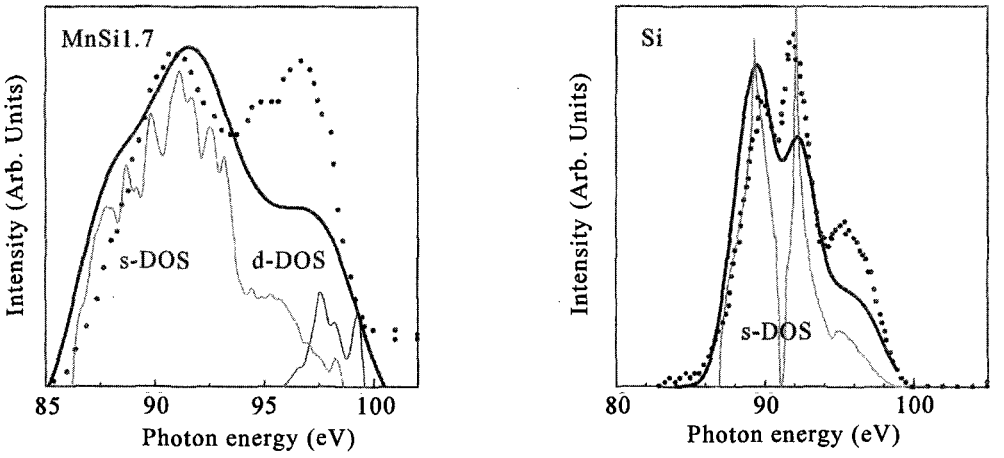


Fig.7 Si $L_{2,3}$: X-ray emission spectrum. The dots line shows experimental results by J. Wang *el al.* and solid line present theoretical results. The s- and d- components of DOS in the valence band are shown for comparison.

accompanies transition from s- and d-character states in the valence band to the core p state. In order to compare with the experiment, the calculated results have been shifted and the intensity has been normalized to agree both calculated and experimental spectra as a whole. Calculated results for $MnSi_{1.7}$ and Si are shown in Fig.7 together with the experiment. In Fig.7 s- and d-character DOS are also shown for comparison. Experimentally the spectrum of $MnSi_{1.7}$ has two peaks ~91 eV and ~97 eV. The spectrum of Si has double peaks ~89 eV and ~92 eV and a wide shoulder peak from ~94 to ~98 eV. The overall line shape of theoretical spectra is in reasonable agreement with the experiment. The peak of valence band of $MnSi_{1.7}$ is due to th Si-Mn bond formation. Valence bands consist of many parabolic-like bands with Si-s, p orbital and the flat Mn-d orbital character. In Si bulk spectrum the line width is small compared to that in $MnSi_{1.7}$ spectrum: the hybridization of Mn and Si orbital in $MnSi_{1.7}$ causes the broadening.

It is noted that the crystal structure of the sample $MnSi_{1.7}$ for the X-ray emission measurement was not identified clearly in the work of Wang *et al.*, though the lattice constant of $Mn_{15}Si_{26}$ was mentioned in the table [7]. In the present work the calculated results in $Mn_{15}Si_{26}$ have been shown, though calculated results in Mn_4Si_7 are almost the same.

Thus, the experimental and calculated results of Si $L_{2,3}$-edge X-ray emission spectra in both $MnSi_{1.7}$ and Si agree well with shapes and width. This indicates the present work on the electronic structure is reliable.

5.CONCLUSIONS

We have investigated the electronic structure of Mn_4Si_7 and $Mn_{15}Si_{26}$ by means of FLAPW method. By minimizing the total energy to the lattice parameter of Mn_4Si_7, theoretical lattice constants have been determined. The determined lattice constant agrees well with the experimental one: the differences are smaller than 0.2 %. Then the electronic structure and density of states are calculated and feature of the atomic origin for the various bands is clarified. Then the result is used to calculate Si $L_{2,3}$ X-ray emission spectra of $MnSi_{1.7}$ together with that of the bulk Si for comparison. The calculated results explain well the experimental spectra in both $MnSi_{1.7}$ and Si.

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