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Cite as: AIP Advances **6**, 065317 (2016); https://doi.org/10.1063/1.4954667
Submitted: 18 May 2016 . Accepted: 11 June 2016 . Published Online: 17 June 2016

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AIP ADVANCES **6**, 065317 (2016)

The structure and electronic properties of hexagonal Fe_2Si

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(Received 18 May 2016; accepted 11 June 2016; published online 17 June 2016)

On the basis of first principle calculations, we show that a hexagonal structure of Fe_2Si is a ferromagnetic crystal. The result of the phonon spectra indicates that it is a stable structure. Such material exhibits a spin-polarized and half-metal-like band structure. From the calculations of generalized gradient approximation, metallic and semiconducting behaviors are observed with a direct and nearly 0 eV band gap in various spin channels. The densities of states in the vicinity of the Fermi level is mainly contributed from the *d*-electrons of Fe. We calculate the reflection spectrum of Fe_2Si, which has minima at 275nm and 3300nm with reflectance of 0.27 and 0.49, respectively. Such results may provide a reference for the search of hexagonal Fe_2Si in experiments. With this band characteristic, the material may be applied in the field of novel spintronics devices. [http://dx.doi.org/10.1063/1.4954667]

Among the Fe-Si compounds, the β-$FeSi_2$ is a well known compound as it is a Kankyo (environmentally friendly) semiconductor with a 0.8eV indirect band gap.[1] β-$FeSi_2$ has remarkable properties and has been studied extensively in the field of optoelectronic applications.[2,3] In recent years, other Fe-Si compounds also attract considerable attention. For example, tetragonal Fe_2Si with Pm3-m symmetry group and CsCl structure was found at 1974.[4] From the fact that the compound has to be formed under the space weathering condition on airless or meteorite impacts, in 1975 it was predicted that the compound should exist on the lunar surface.[5] Thereafter, it was indeed found in a lunar meteorite of a highland-regolith breccia named as Dhofar 280.[6] This kind of tetragonal Fe_2Si is called hapkeite. A similar isomer, hexagonal Fe_2Si of P3-m1 symmetry group and Ni_2In structure was also found in 1977.[7] It can be formed during quenching.[8] This material, however, has not been well studied yet. Since the Fe-Si compounds (such as β-$FeSi_2$ and FeSi) are useful in electronics, we will investigate the properties of hexagonal Fe_2Si, including its crystal structure, and its magnetic, optical, and band properties. We also present a discussion on its possible applications.

On the basis of density functional theory (DFT),[9,10] we use pseudopotential method of CASTEP (the Cambridge sequential total energy package)[11] with the ultrasoft pseudopotential method[12] and all-electron full-potential electronic structure code of FHI-aims (Fritz Haber Institute ab initio molecular simulations)[13] to calculate the crystal structure and the band structure. We adopt two approximations in the both methods: the local density approximation (LDA) with the CA-PZ form,[14] and the generalized gradient approximation (GGA) with the PBE form.[15] Because when the kinetic energy cutoff exceed 400eV, the change of total energy is less than 1meV/atom, the cutoff energy is set to 450eV. $12 \times 12 \times 12$ k points are taken for calculations in the Brillouin zone (BZ) and use Monkhorst-Pack method of the point distribution.[16] In the all-electronic calculations, The basis set

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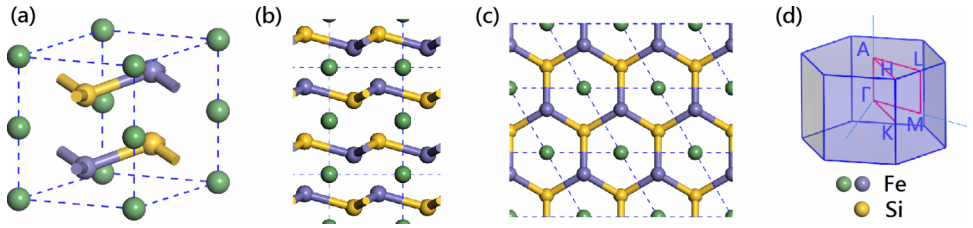

FIG. 1. The crystalline structure of hexagonal Fe_2Si with its primitive cell surrounded by blue dashed line. (a): The hexagonal Fe_2Si belongs to P3-m1 space group. The violet and green balls indicate a different position of Fe atoms. (b,c): Patterns viewed along the [110] and [001] directions, respectively. (d): The Brillouin zone and the lines with high symmetry.

and numerical grids are set to high quality as defined by the "tight" option.[13] In addition, the structural optimization is performed by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method[17] and the convergence tolerances are set to 5.0×10^{-6} eV/atom for energy, 0.01eV/Å for maximum force, 0.02GPa for maximum stress, and 10^{-4}Å for maximum displacement. The phonon spectrum and the optical properties are calculated with the CASTEP code, and for phonons the finite displacement method with the cutoff radius 5.0 Å is used.

The structure of hexagonal Fe_2Si is shown in Fig. 1. It is a hexagonal crystal system and belongs to the P-3M1 space group. There are 4 Fe atoms and 2 Si atoms to form a primitive cell. It is composed with a uneven honeycomb sublattice of components Fe and Si, and a hexagonal sublattice of component Fe, similar to the Ni_2In structure. The optimized lattice parameters obtained with different methods are shown in Table I. The results of experiment and calculations indicate that the symmetry constraints of the lattice parameters are $\alpha = \beta = 90°, \gamma = 120°$ and a = b. From the results, deviations of the optimized values of lattice parameters from those of experiment are less than 3-6% for a and b, less than 5-9% for c, and less than 3% for c/a. These deviations are probably caused by the higher temperature in experiment.

The magnetic properties of Fe_2Si are similar to the materials of Ni_2In structure. It exhibits ferromagnetism, like MnRhAs and MnCoAs, which are calculated by Korringa-Kohn-Rostoker (KKR) method and the KKR-CPA (coherent potential approximation) with magnetic moments 3.31 and 3.25 per cell, respectively.[18] By means of Mulliken population analysis, we found that the magnetic moments of Fe atoms in the upper and lower layers of the hexagonal sublattices are 2.78 μB and 2.50 μB obtained from the GGA and LDA methods, representatively. For the Fe atoms in the middle layer of the hexagonal sublattices, the moments are 0.04 μB from GGA and 0.12gμB from LDA. For the Fe atoms in the honeycomb sublattices, the moments are 0.66 μB from GGA and 0.58 μB from LDA. The moments of Si atoms are 0.06 μB from GGA and 0.04 μB from LDA. This indicates that the main contribution of the magnetic moments of Fe_2Si comes from the Fe atoms in the upper and lower layers of the hexagonal sublattices. The magnetic moments of a primitive cell with the hexagonal Fe_2Si structure are shown in Table I. Such a distribution of the magnetic moments is similar to that of the ferromagnetic crystal with Ni_2In structure.[18] It is also worth noting that some of Ni_2In structure exhibit magnetic-field-induced martensite transformation effects and martensite phase transformation to orthogonal structure occurs in decreased temperature.[19,20] In order to further discuss the stability of Fe_2Si, the phonon dispersion relation is calculated and the stability of the structure is examined by the absence of imaginary-frequency phonon modes. The

TABLE I. The cell parameters and cell moments of primitive cell in hexagonal Fe_2Si structure.

	Experiment	GGA	GGA-FHI	LDA	LDA-FHI
a = b	4.05	3.90	3.93	3.81	3.85
c	5.09	4.80	4.82	4.69	4.72
c/a	1.26	1.23	1.23	1.23	1.23
v	72.30	63.23	64.47	58.96	60.59
cell moments	–	4.020	4.040	3.689	3.710

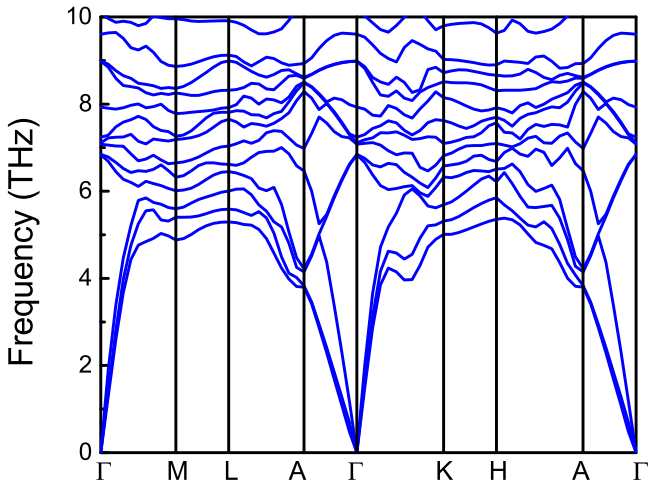

FIG. 2. The phonon dispersion relation of Fe_2Si.

phonon dispersion relation for Fe_2Si is shown in Fig. 2. It indicates that the hexagonal structure of Fe_2Si is stable.

We use the pseudopotential method together with GGA to calculate the band structure and the partial densities of states (PDOS) of hexagonal Fe_2Si. The results are displayed in Fig. 3. One of the notable characteristics of hexagonal Fe_2Si is that the band diagram has a half-metal-like structure. Compared with the band structures of the non-polarized β-$FeSi_2$ calculated with the augmented spherical wave method[21] and the non-polarized FeSi calculated with the linear augmented-plane-wave method,[22] the increase of the proportion of iron atoms in hexagonal Fe_2Si causes the spin polarization. From Fig. 3 we can observe a zero direct band gap in spin-down band at the L point of BZ (the band gap of β-$FeSi_2$ and FeSi are 0.44eV and 0.11eV, respectively[21,22]). It is a half gapless semiconductor. When the band structure was calculated with LDA, we can also observe a −0.3 eV negative band gap in spin-down band at the L point. In addition, the results from the all-electronic calculation together with the method of +U (1eV) are similar to those from the pseudopotential method. The band gaps from different methods are shown in Table II.

These results indicate that this material is a semimetal with the negative gap or gapless band in spin-down subband. Because with different methods the top of the valence band (VBT) and to the

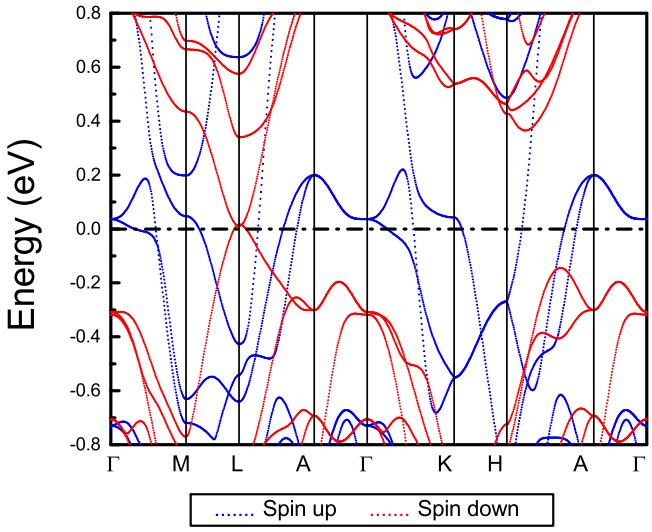

FIG. 3. Electronic band structure of hexagonal Fe_2Si calculated by using GGA functional and pseudopotential method.

TABLE II. The valence band top (VBT), the conduction band bottom (CBB) and the band gap of hexagonal Fe_2Si obtained from different calculation methods.

Methods	VBT(eV)	CBB(eV)	Band gap(eV)
GGA	0.01	0.02	−0.01
GGA-FHI	0.02	−0.06	0.08
GGA+U (1eV)	0.38	−0.03	−0.41
LDA	−0.38	−0.10	−0.28
LDA-FHI	−0.37	−0.13	−0.24
LDA+U (1eV)	0.20	−0.08	0.28

bottom of the conduction band (CBB) have a very small overlap or have a little band gap near the Fermi energy, this property may need further experimental validation. On the other hand, the spin up subband manifests metallic behavior. As the spin down subband shows the gapless behavior, the hexagonal Fe_2Si should belong to a spin gapless half-metal. Since the excitation energy in quantum dots made of a negative-band-gap or gapless semiconductor can be regulated with the methods of changing the size or doping,[23] and some materials with a negative-band-gap exhibit a charge-density wave and excitonic insulator phase,[24] such a spin gapless half-metal has potential application for controlling electron spins in spintronics.

The results of PDOS from different calculation methods show the similar behaviour. Figure 4, shows the contributions to the DOS from different spins and from different atoms calculated from GGA together with the pseudopotential method. Near the Fermi energy the DOS are significantly contributed from the *d*-electrons of Fe atoms and the contributions from *s* or *p* states are ineffective. It also illustrates that the half-metal-like properties of the negative-band-gap comes from the *d*-electrons of Fe atoms. At the same time, the electrons from Si atoms play a main role in the covalent bonds. Corresponding to the results of the band structure near the Fermi energy which shows a small overlap of the spin down subbands as shown in Fig. 3, the total DOS of spin down subbands have a nonzero minimum which is slightly deviated from the Fermi energy. In our previous work, the PDOS of iron-containing compound – 2D pt-Fe_2S also exhibits similar characteristics.[25]

Similarly to the hapkeite, hexagonal Fe_2Si has not been found in the Earth. However, hapkeite could be synthesized under the space weathering in airless environment and on the effect of meteorite impact. Since the hapkeite was found in lunar meteorites(Dhofar 280), it also contains Fe and Si elements as FeSi and $FeSi_2$ compounds,[6] the difference between hexagonal Fe_2Si structure and the hapkeite as well as the possibility of mutual transformation are worth further study.

Based on conventional technologies, the main methods for the study of mineral compositions on the lunar surface include reflectance spectroscopy, thermal radiation *etc*. Therefore, we calculate the reflectivity of plane polarized light with polarizations in the 100, 010 and 001 directions from the surface of hexagonal Fe_2Si. Because of the small anisotropy of the lattice structure and

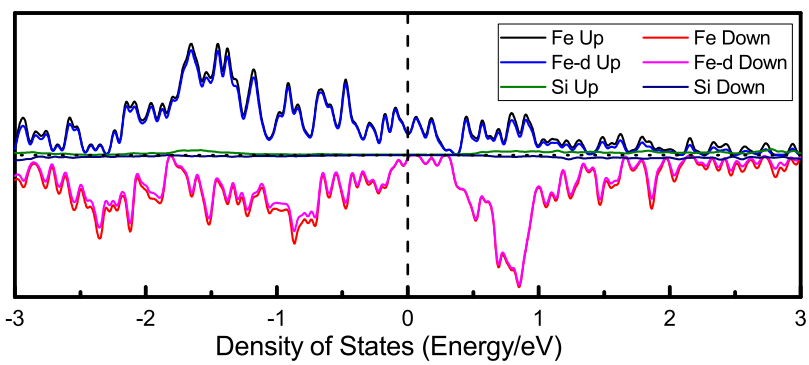

FIG. 4. Partial densities of states (PDOS) of hexagonal Fe_2Si calculated by using GGA pseudopotential method.

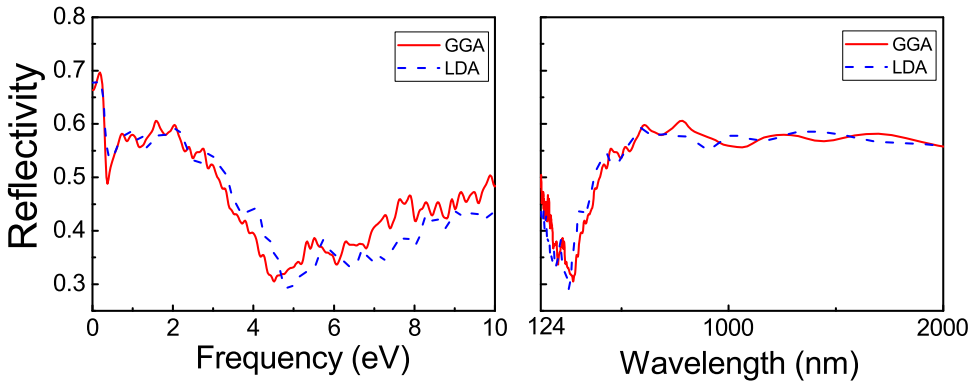

FIG. 5. The reflectance spectroscopies of hexagonal Fe_2Si are calculated by the method of polycrystal.

the electronic bands, the results for different polarization directions are similar. The reflectance spectroscopies of hexagonal Fe_2Si are calculated in the case of polycrystal (average over all crystalline directions) and the results are shown in Fig. 5. With the GGA calculation, the reflectivity of hexagonal Fe_2Si has a relative minimum at 4.51eV (275nm) with reflectance of 0.27 in the range of near infrared to ultraviolet (2000-124nm), it also has a relative minimum at 0.37eV (≈3300nm) with reflectance of 0.49 and a relative maximum 0.60 between these two minima. The results from the LDA calculation are similar. This is different from the results of β-$FeSi_2$ and FeSi, for which there are significant differences between the LDA and GGA calculations. In β-$FeSi_2$, there are a relative minimum 0.45 at 3eV and a relative maximum 0.54 at 1eV.[26,27] In FeSi, there are 2 relative minimum 0.25 and 0.12 at 4eV and 10eV respectively, and a relative maximum 0.35 at 7eV between them.[28] The differences of the reflection spectrum may be used for the search of hexagonal Fe_2Si on the lunar surface or other meteorites.

In conclusion, we use first principles calculation to study the structure, lattice parameter, phonon spectrum and reflectance spectroscopy of hexagonal Fe_2Si. From the results of the band structure and the PDOS, it is a ferromagnetic crystal and has a spin-polarized half-metal-like band structure and a near 0eV band gap, which is mainly contributed from the spin-down d-electrons of Fe atoms. Because of these characteristics, it may be used in spintronics. Finally, the reflection spectra of hexagonal Fe_2Si are calculated and compared with other Fe-Si compounds. The distinct reflection spectra provide a reference for the search of the compound in the future, because it is possible that the hexagonal Fe_2Si will symbiont with other Fe-Si compounds under space weathering or meteorite impacts. Whether the hexagonal Fe_2Si exists in the space environment or coexists with other Fe-Si compounds is worth further study.

The work is supported by the Science and Technology Development Fund of Macau (020/2014/A1, 039/2013/A2), and the State Key Programs for Basic Research of China (Grant No. 2011CB92 2102), and by National Foundation of Natural Science in China of Grant Nos. 61076094 and 10874071.

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