

STRUCTURAL AND ELECTRONIC PROPERTIES OF XSi_2 ($X = Cr, Mo, AND W$)

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Received November 14, 2014

The structural and electronic properties of metal silicides XSi_2 ($X = Cr, Mo, and W$), which crystallize in tetragonal structure, are investigated systematically using the first-principle density functional theory. The total energies are computed as a function of volume and fitted to the Birch equation of state. The ground-state properties such as equilibrium lattice constants, a_0 and c_0 , bulk modulus B , its pressure derivative B' , and the density of states at the Fermi level, $N(E_F)$, are calculated and compared with other experimental and theoretical results, showing good agreement. The calculated band structure indicated that XSi_2 compounds are semimetallic in nature. From the present study, we predict the structural and electronic properties of $CrSi_2$ in the tetragonal phase and indicate that $CrSi_2$ is energetically more stable than $MoSi_2$ and WSi_2 . Analyzing the bonding properties of the three metal silicides, we observe that WSi_2 has a strong covalent bonding due to $W 5d$ electrons.

DOI: 10.7868/S004445101507010X

1. INTRODUCTION

Metal silicides have been subjected to research due to their attractive properties, including superb strength at high temperature, high oxidation and corrosion resistance, and a relatively low density [1]. Many properties of metal silicides are related to the electronic structure, and so far comparatively less attention has been paid to studying the local and partial densities of their states. In their bonding properties, the role of the metal d wave function has not been in the focus of attention [2]. Extensive research has been done on the silicides related to their metallic behavior. On the other hand, semiconducting silicides are less studied materials. Chromium disilicide ($CrSi_2$) is one of the semiconducting silicides that has potential applications in optoelectronic devices and infrared detectors [3, 4]. Molybdenum disilicide ($MoSi_2$) has been studied by first-principle density functional theory for its electronic structure and mechanical properties (see [5] and references therein). The authors of [5] focused on bonding characteristics

and confirmed that the hardness and ductility of $MoSi_2$ materials is mainly due to Si–Si interactions. Elastic constants and structural properties of Mo and $MoSi_2$ have been calculated in [6] by using the linear muffin tin orbital (LMTO) method. Experimental study of specific heat of $MoSi_2$ has been reported in [7]. In [8], the electronic structure of bulk refractory metal disilicides VSi_2 , $TaSi_2$, and $MoSi_2$ was studied using photoelectron spectroscopy with synchrotron radiation. The electronic structure of Mo – Si was investigated in [9] using valence-band X-ray photoelectron spectroscopy (VBXPS) and density functional theory. The differences between the VBXPS spectra for $MoSi_2$, Mo_5Si_3 , and Mo_3Si are explained in terms of various hybridizations involving $Si-p$ and $Mo-d$ states.

The electronic structure of $MoSi_2$, Mo_5Si_3 , $NiSi_2$, and Ni_2Si transition metal silicides was studied by authors of Ref. [2] both experimentally and theoretically. They suggested that the chemical bonding in silicides is mainly due to the extension of the metal “ d ” wave function and local structure. The linear augmented plane wave (LAPW) method has been applied to calculate the valence electron contribution to the total energy of the tetragonal and hexagonal phases of metal silicides

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in the local density approximation in [10]. The energy bands, projected densities of states, and cohesive energy of WSi_2 (Tungsten disilicide) were calculated in [11] using a selfconsistent pseudopotential method. Fermi surfaces (FSs) are related to the energy band theory and are important for characterizing metals and semiconductors; various properties of metals are also determined by the shape of the FS. The FS of tungsten silicides has been determined from a semirelativistic self-consistent band calculation in [12]. To the best of our knowledge, the experimental lattice constant of CrSi_2 in the tetragonal phase has not been reported yet. We have performed a calculation and studied the role of metal and silicon bands in a band structure and bonding properties of XSi_2 ($X = \text{Cr}, \text{Mo}, \text{and W}$) within the generalized gradient approximation (GGA) and local spin density approximation (LSDA).

2. METHOD OF CALCULATION

The calculations have been performed in the framework of density functional theory (DFT). The full potential (FP) LAPW method as implemented in the WIEN2k code [13] has been used. The exchange and correlation effects were treated using PBE-GGA [14], WC-GGA [15], and LSDA [16] calculations. The local density approximation (LDA) is the simplest approximation for the functional, it is local in the sense that the electron exchange and correlation energy at any point in space is a function of the electron density at that point only. Generalizing this to spin-polarized systems results in the LSDA. The GGA and hybrid approximations have reduced the LDA errors of atomization energies of a standard set of small molecules.

The energy eigenvalue convergence has been achieved by expanding the basis function up to $R_{MT}K_{max} = 7$, where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest \mathbf{k} vector in the plane-wave expansion. The valence wave functions inside the spheres are expanded up to $l_{max} = 10$ while the charge density is Fourier-expanded up to $G_{max} = 12$. The self-consistent calculations converge when the total energy of the system is stable within 10^{-4} Ry. The energy to separate the core and valence state is -6.0 Ry. A dense mesh of 1000 \mathbf{k} points and the tetrahedral method [17] have been used for the Brillouin zone integration. The total energies are fitted to the Birch equation of state [18].

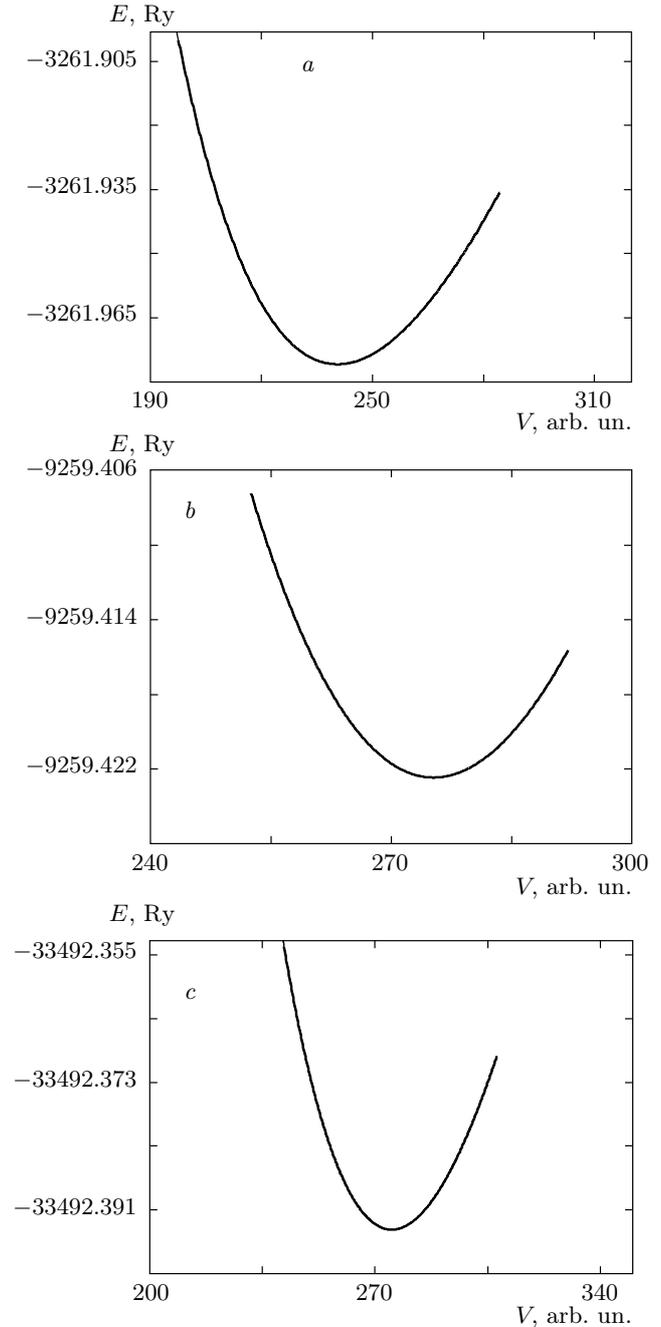


Fig. 1. Variation of the total energy with the volume of (a) CrSi_2 , (b) MoSi_2 , and (c) WSi_2

3. RESULTS AND DISCUSSION

3.1. Structural properties

The electronic band structure calculations are performed to obtain the total energy of the XSi_2 ($X = \text{Cr}, \text{Mo}, \text{and W}$) metal silicides using the first-principle FP-LAPW method. The variation of the total en-

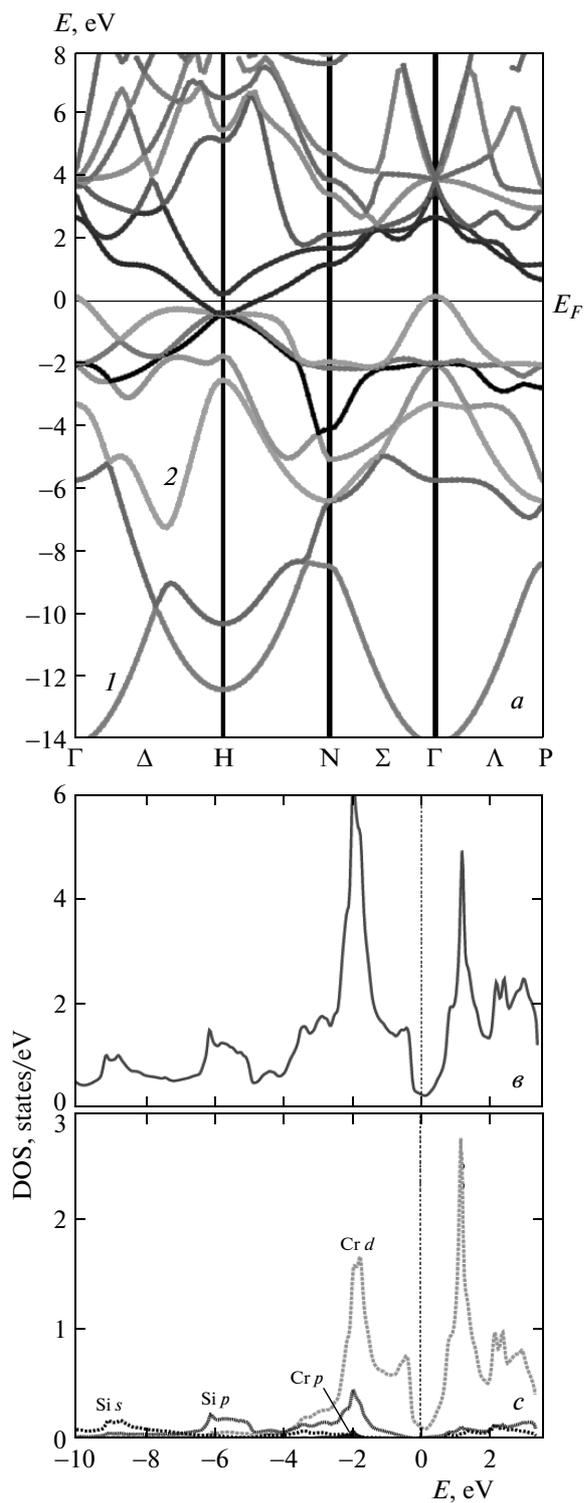


Fig. 2. (a) Band structure and density of states, (b) total and (c) partial, of CrSi_2

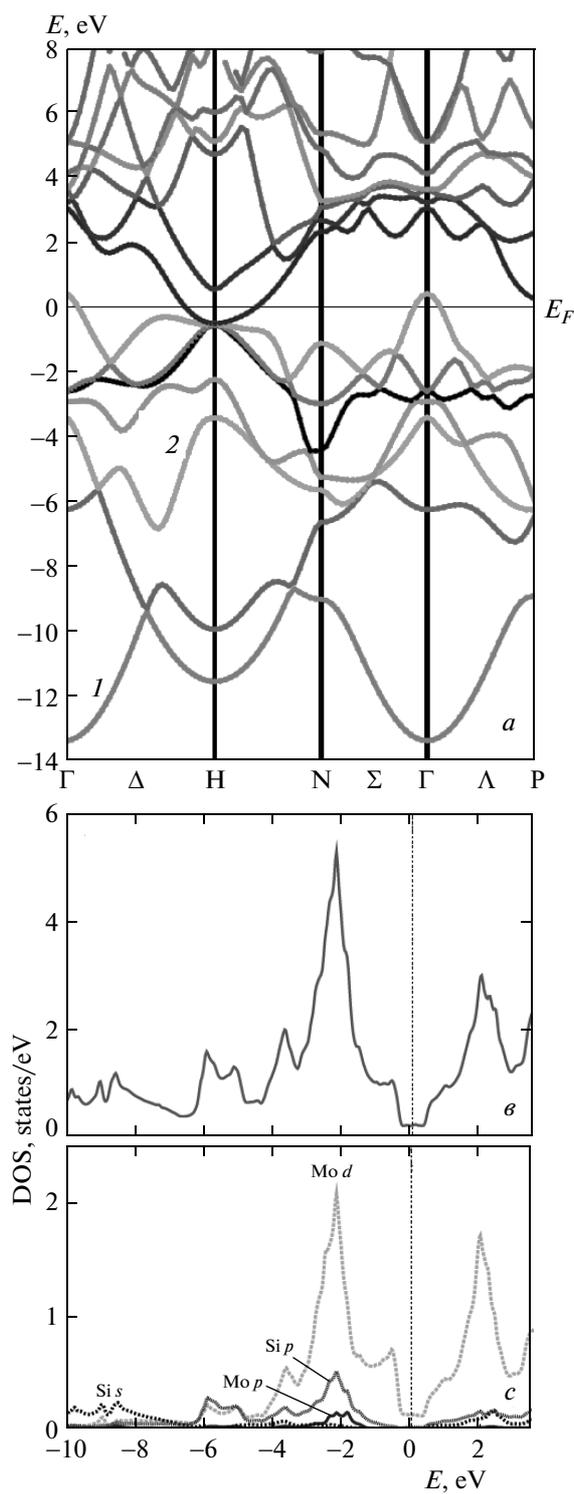


Fig. 3. (a) Band structure and density of states, (b) total and (c) partial, of MoSi_2