

Article

Optimal Location of Vanadium in Muscovite and Its Geometrical and Electronic Properties by DFT Calculation

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Academic Editor: Shifeng Dai

Received: 26 December 2016; Accepted: 17 February 2017; Published: 24 February 2017

Abstract: Vanadium-bearing muscovite is the most valuable component of stone coal, which is a unique source of vanadium manufacture in China. Numbers of experimental studies have been carried out to destroy the carrier muscovite's structure for efficient extraction of vanadium. Hence, the vanadium location is necessary for exploring the essence of vanadium extraction. Although most infer that vanadium may substitute for trivalent aluminium (Al) as the isomorphism in muscovite for the similar atomic radius, there is not enough experimental evidence and theoretical supports to accurately locate the vanadium site in muscovite. In this study, the muscovite model and optimal location of vanadium were calculated by density functional theory (DFT). We find that the vanadium prefers to substitute for the hexa-coordinated aluminum of muscovite for less deformation and lower substitution energy. Furthermore, the local geometry and relative electronic properties were calculated in detail. The basal theoretical research of muscovite contained with vanadium are reported for the first time. It will make a further influence on the technology development of vanadium extraction from stone coal.

Keywords: vanadium; muscovite; stone coal; substitution; geometry; electronic property; DFT

1. Introduction

Vanadium (V), as a steel alloy additive, is widely used in refining high-strength steels, titanium–aluminum alloys and oxidation catalysts [1], whilst its polyvalence gives it potential for development of a vanadium redox battery [2,3]. In China, V-bearing stone coal is a significant source to product vanadium compounds. The gross reserves of stone coal in China are about 61.88 billion tons, in which the V grade generally ranges from 0.01% to 1.3% [1,4]. The process mineralogy shows that the main minerals in stone coal include quartz (SiO₂), muscovite (KAl₂(Si₃Al)O₁₀(OH)₂), calcite (CaCO₃), and pyrite (FeS₂). Most V in stone coal exists in the dioctahedral sheet of mica-group minerals, such as muscovite [5]. Most investigations of V extraction from stone coal essentially aim to destroy the structure of muscovite to liberate V. In the traditional process, roasting and leaching play a significant role in increasing the leaching rate of V, while the mechanism study of them needs to clarify the target site of the high temperature destruction and hydron exchange. The accurate location of V in muscovite lattice is indispensable for further exploring the essence of V extraction from stone coal. Many V-extracting experiments of stone coal have put forward the inference that V may substitute

trivalent aluminium (Al) as the isomorphism in muscovite, based on the similar ratio of charge to atomic radius [6,7], which is similar to the cation substitutions of Al^{3+} by Mg^{2+} and Fe^{3+} in the octahedral sheet. However, there is not enough evidence to sustain this point in direct experimental characterization or instrument tests, due to the complexity of natural V-bearing muscovite, which is finely grained and poorly crystallized in stone coal [8]. Therefore, the introduction of simulating calculation by quantum chemistry makes it possible to distinguish the optimal location of V and obtain the related physical and chemical properties.

In recent years, the ab initio methods or density functional theory (DFT) with periodic boundary conditions and pseudopotential have applied to the study of crystallographic, elastic and thermal properties of aluminosilicate [9–12]. Especially, surfaces and interlayers of phyllosilicate were studied by DFT calculations [13–15]. The quantum chemical calculations can identify the most steady state by comparing the total energies of different structures, and analyzing the interaction between V and oxygen in the lattice, which further affects the related physical and chemical properties of muscovite.

In this paper, we presented a detailed DFT study of muscovite modified by the substitution of V, and resolved its optimal location in the view of energy and local structure. In addition to its reliable crystallography, we also revealed the difference of the muscovite's electronic properties and the bond nature as the V exists. Hence, it can provide a theoretical basis and experimental instruction for further destruction of V–O bond and the process of V dissolution from muscovite.

2. Methods

2.1. Structure and Models

Initial atomic coordinates for the crystal structure of muscovite is taken from the Catti et al. [16] basing on powder neutron diffraction, where the lattice parameters are $a = 5.2108 \text{ \AA}$, $b = 9.0399 \text{ \AA}$, $c = 20.021 \text{ \AA}$, and $\beta = 95.76^\circ$. The ideal chemical formula of muscovite is $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$. The unit cell of muscovite is stacked by two 2:1 layers, which contains two tetrahedral sheets (T) and one octahedral sheet (O) (Figure 1a) [13,16]. The tetrahedral sheet consists of many SiO_4 units bonded with each other by the triangular basal oxygens of the tetrahedron. Six SiO_4 units form a ring of quasi-hexagonal symmetry (Figure 1b). Then, those quasi-hexagonal rings bond with each other, forming a plane of infinite extension. The central atoms of O sheets are six-coordinated with octahedron geometry. In detail, the octahedral polyhedron is formed by four oxygens, which belong to the apices of T sheets and two vertices which are hydroxyl groups in the center of the quasi-hexagonal ring. The muscovite is dioctahedral phyllosilicate series and only two-thirds of the octahedron are occupied in O sheets. Meanwhile, the presence of substitution of Al(III) for the quarter of Si(IV) (tetravalent silicium) results in a net negative charge that is compensated by a sheet of K cations between two layers. All sheets are parallel to the (001) plane. Thus, it is necessary to build a muscovite model with explicit arrangement of Al for comprehensive investigation of V substitution.

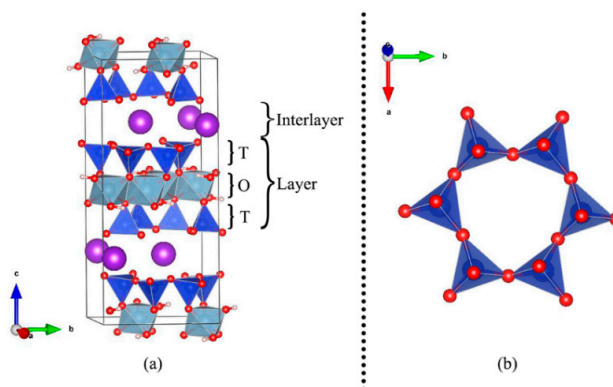


Figure 1. The structure of (a) unit cell and (b) quasi-hexagonal ring of SiO_4 units.

The isomorphic substitutions in 2:1 dioctahedral phyllosilicates show a considerable short-range order but no long-range order [17,18]. Previous theoretical and experimental studies on muscovite found an ordered distribution of the cations in the *T* sheet with the Loewenstein Al-avoidance rule [19–21]. This distribution was also investigated by combining quantum mechanics methods with empirical models to reduce the number of different atomic configurations, which consume vast computing resources [22,23]. In many pieces of literature, the arrangements are often presumed without direct supporting evidence [24]. For getting the reliable muscovite model, we elucidated any such effects by comparing several Al arrangements.

Considering the one unit cell of muscovite with 84 atoms, doubling the size of the supercell would make DFT calculations prohibitively expensive. We consequently used one unit cell for muscovite model calculations. In order to build the conventional unit cell, we assumed an equal tetra-coordinated aluminum (Al^{IV}) concentration in each layer. Namely, there is only one Al^{IV} to distribute among four sites in *T* sheets. For simplicity, we artificially rebuilt the crystal symmetry in the models, in which the Al^{IV} substitute in the form of center-symmetry (Figure 2a). Albeit maintaining symmetry does not consider all possible aluminum distributions in the real minerals, it is a good initial model compared to experimental observations. Finally, there are sixteen calculation configurations to elect the optimal muscovite model.

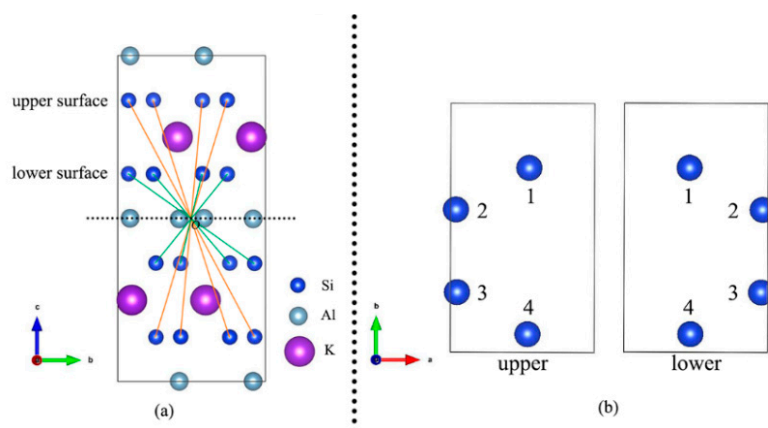


Figure 2. (a) The Al^{IV} substitution abided by center-symmetry; (b) the label of upper surface and lower surface beside interlayer.

Then, a $2 \times 1 \times 1$ supercell containing 168 atoms was generated by the unite cell of the optimal muscovite model. The V substitution was achieved by replacing Si or Al in the supercell. Thus, we considered three categories for V substitution: (a) octahedral Al; (b) tetrahedral Al; and (c) tetrahedral Si. The V substitution in the actual muscovite presents at a relatively low level, and we only substituted the single 2:1 layer with one V atom. Thus, we identified the optimal location of V.

2.2. DFT Calculations

The DFT calculations were performed with the Vienna ab initio simulation package (VASP) developed for periodical systems [25,26]. The exchange-correlation functional used the Perdew-Burke-Ernzerhof (PBE)-version of the generalized gradient approximation (GGA) [27,28] and the plane-wave basis set used projector augmented waves (PAW) [29,30]. These methods have provided close lattice parameters to experimental values of phyllosilicates [31]. In detail, the tested kinetic energy cutoff value of 800 eV and a $(8 \times 4 \times 2)$ Γ -point centered *k*-points mesh were accomplished to truncate the plane-wave basis in the high-precision calculations of muscovite model. Considering the double size of the *a*-axis in the supercell, the *k*-points were reduced to $(4 \times 4 \times 2)$ in the calculations of V substitution. Meanwhile, other parameters were remained. Full geometry optimization calculations were performed in which all structural parameters were relaxed without constraint of the space group

symmetry. Namely, the space group was *P1*. All calculations were convergent until the total energy change of 10^{-4} eV and residual forces of 0.05 eV/Å, respectively. With these parameters, converged total energies and lattice vectors were obtained.

3. Results and Discussion

3.1. Muscovite Model

We defined the surfaces beside interlayer with upper surface (U) and lower surface (L) (Figure 2a). Every surface have four different substitutable sites, which were labelled 1–4 (Figure 2b). The sixteen possible configurations were identified by combination, like C_{UL} , and the calculated crystallographic parameters were compared with experimental values in Table 1.

Table 1. The calculated crystallographic parameters of sixteen configurations.

C_{UL}	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	E (eV)
Exp	5.211	9.040	20.021	90.00	95.76	90.00	-
C_{11}	5.293	9.122	20.267	90.00	95.83	90.00	0.025
C_{12}	5.285	9.134	20.270	89.90	95.88	90.09	0.072
C_{13}	5.292	9.124	20.261	90.00	95.83	90.00	0
C_{14}	5.284	9.136	20.266	89.95	95.88	90.09	0.089
C_{21}	5.285	9.134	20.270	90.10	95.88	89.91	0.077
C_{22}	5.278	9.145	20.275	90.00	95.94	90.00	0.187
C_{23}	5.284	9.136	20.266	90.05	95.88	89.91	0.091
C_{24}	5.278	9.148	20.267	90.00	95.94	90.00	0.148
C_{31}	5.292	9.124	20.261	90.00	95.83	90.00	0
C_{32}	5.284	9.136	20.266	89.95	95.88	90.09	0.093
C_{33}	5.293	9.122	20.267	90.00	95.83	90.00	0.027
C_{34}	5.285	9.134	20.270	89.90	95.88	90.09	0.072
C_{41}	5.284	9.136	20.266	90.05	95.88	89.91	0.091
C_{42}	5.278	9.148	20.267	90.00	95.94	90.00	0.147
C_{43}	5.285	9.134	20.270	90.10	95.88	89.91	0.078
C_{44}	5.278	9.145	20.275	90.00	95.94	90.00	0.186

E is the relative total energy based on the lowest total energy, C_{13} (C_{31}), thus the energy of C_{13} (C_{31}) was returned to zero.

For muscovite, we obtained fair agreement within the estimated experimental uncertainty of the lattice parameters, which was determined in powder neutron diffraction experiment. The relative deviations of cell parameters were reported (Figure 3). After substitution, the a -axis, b -axis and c -axis expand less than 1.42%, 1.05% and 1.23%, respectively. Simultaneously, the average calculated Si–O distance (1.641 Å) and Al–O distance (1.944 Å) have minor differences to the experimental bond length (1.643 Å, 1.943 Å, respectively). While the average calculated O–H distance (0.972 Å) is 2.6% longer than the experimental values (0.947 Å), it can be resulted from the dangling nature of O–H and the hydrogen bonds of H atoms formed with the nearest O atoms [11]. Thus, these insignificant differences prove the reliability of these DFT calculations. In the sixteen configurations, the relative deviations and relative total energy of C_{13} are similar to C_{31} , the C_{24} is similar to C_{42} , and the C_{12} and C_{21} are similar to C_{34} and C_{43} , respectively. Thus, they can be divided into six categories shown in Figure 3. It suggests that the Al-substitutions of the 1 and 3 sites or 2 and 4 sites of Si in each T sheet are equivalent. It can be ascribed to the similar environment of Si before substitution.

The most stable case is C_{13} and C_{31} , where Al atoms beside interlayer prefer a “W” shape for the longer Al–Al distance (Figure 4). However, all categories differ in total energy by less than 0.2 eV/f.u. Such slight energy differences between the minimum energy and other suboptimum structures demonstrate thermal disorder of the Al distribution in this material [32]. As a model configuration, an Al distribution with the lowest total energy is assumed, C_{13} , with $a = 5.292$ Å, $b = 9.124$ Å, $c = 20.261$ Å, and $\beta = 95.83^\circ$.

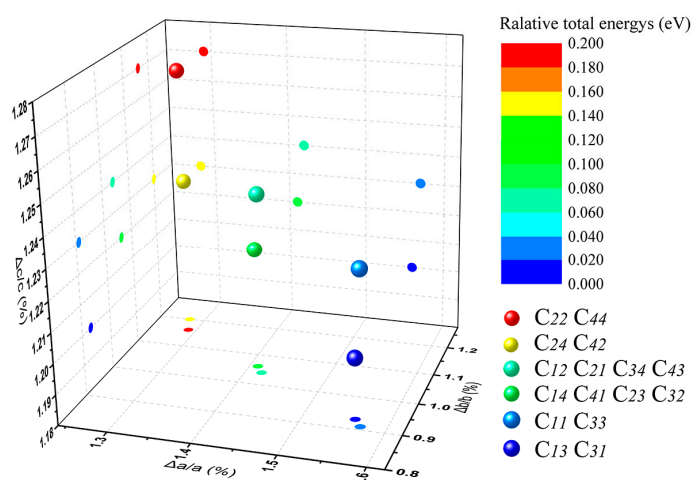


Figure 3. The relative deviations of cell parameters and total energy of sixteen configurations.

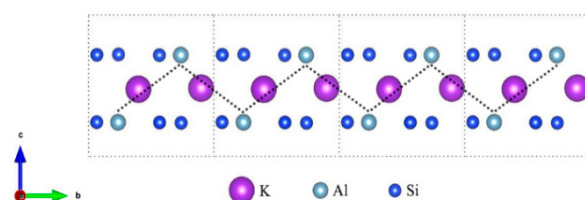


Figure 4. One layer of the muscovite model along the *a*-axis.

3.2. Optimal Location of Vanadium and Local Geometry

The dissociation and liberation of cation polyhedron in the muscovite need to absorb enough energy. However, the different cations with different polyhedrons reflect different inflexibility. For instance, the Si–O tetrahedral is more stable than the Al–O octahedral and it is difficult to be destroyed because of the hard Si–O bond and the ring of the quasi-hexagonal. Thus, the location of V will directly decide whether the V existing in muscovite is easy to be extracted or not. Hereinafter, we compared the different locations where V substituted in the aspects of energy and structure.

Due to the reduced overall symmetry for the Al substitution, the Si–O tetrahedral sites are now split into three non-degenerate types (Figure 5). In total, we calculated the five cases of V substitution in the $2 \times 1 \times 1$ supercell of muscovite. The V substitution assumes the reaction:



where M_O is the original muscovite and M_S is the muscovite with V substitution. V is the vanadium atom and Si(Al) is the silicium or aluminum atom replaced by V. Thus, the substitution energy (E_S) can be defined by the formula:

$$E_S = E[M_S] + E[\text{Si(Al)}] - E[M_O] - E[V] \quad (2)$$

where $E[M_S]$ is the total energy of the muscovite with V substitution. $E[M_O]$ is the total energy of the original muscovite. $E[\text{Si(Al)}]$ and $E[V]$ are the individual ground state energies per atom of Si or Al and V, respectively. Therefore, the negative value of E_S means that this reaction can occur spontaneously. In contrary, the positive value of E_S means that this reaction can not occur spontaneously.

The values of the cell parameters and substitution energies of the five configurations were displayed in Table 2. The calculated cell parameters expand in the *c*-axis with respect to previous model values. Meanwhile, it presents a slight difference within the substitution of non-degenerate

Si–O tetrahedral, but a non-ignorable difference between three categories. The substitution of tetra-coordinated silicon (Si^{IV}) and tetra-coordinated aluminum (Al^{IV}) to V present a larger value of c than hexa-coordinated aluminum (Al^{VI}). It implies that the substitution of Al^{VI} to V lead to a smaller expansion. Furthermore, the increasing order of substitution energy: $\text{V}[\text{Al}^{\text{VI}}] \ll \text{V}[\text{Si}^{\text{IV}}]_2 < \text{V}[\text{Si}^{\text{IV}}]_1 < \text{V}[\text{Al}^{\text{IV}}] < \text{V}[\text{Si}^{\text{IV}}]_3$.

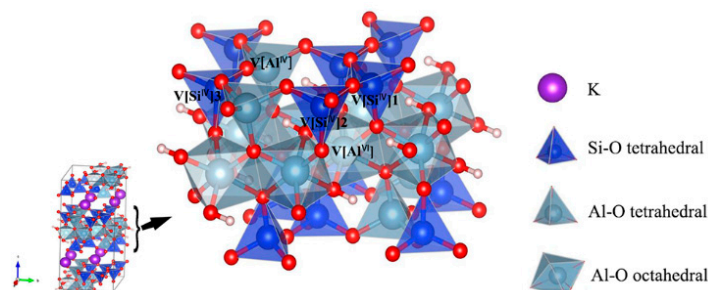


Figure 5. The substituted location in muscovite.

Table 2. The cell parameters and substitution energies of five configurations.

Config	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	E_s (eV)
Model	10.584	9.124	20.261	90.00	95.83	90.00	–
$\text{V}[\text{Al}^{\text{VI}}]$	10.543	9.124	20.358	90.01	95.73	90.00	–1.228
$\text{V}[\text{Al}^{\text{IV}}]$	10.553	9.130	20.376	90.01	95.73	90.00	–0.344
$\text{V}[\text{Si}^{\text{IV}}]_1$	10.576	9.143	20.416	90.00	95.74	90.00	–0.434
$\text{V}[\text{Si}^{\text{IV}}]_2$	10.571	9.145	20.417	90.00	95.77	90.01	–0.519
$\text{V}[\text{Si}^{\text{IV}}]_3$	10.570	9.147	20.415	89.97	95.73	90.03	–0.340

Figure 6 presents the bond distances and angles of the local geometry after substitution. For the Si^{IV} site, the resulting V–O bond lengths are increased by a maximum of 0.174 Å resulting from the larger ionic radius of V compared to Si. However, the bond lengths of neighboring tetrahedra show a slight difference of less than 0.01 Å for the pure tetrahedral structure. Consequentially, the hard bonds of Si–O tetrahedral slightly pull the oxygen atom out of the framework into the interlayer caused by the expansion of the V–O tetrahedral and decrease the inter-tetrahedral bond angles about 2.2°–8.3°. For the Al^{IV} site, the V substitution shows the similar behavior to the Si^{IV} site. In detail, the resulting V–O bond lengths are increased about 0.117–0.138 Å, and the inter-tetrahedral bond angles decrease by about 3.0°–7.3°. For the Al^{VI} site, the resulting V–O bond lengths are increased by maximum of 0.111 Å, and the inter-octahedral angles are changed less than 1.1°. Thus, the substitution in octahedrals presents a smaller expansion than in tetrahedrals due to the plasticity of Al–O octahedrals, which can endure a larger deformation.

In tetrahedral substitution, the shift of bridging oxygens between tetrahedrons along with the c -axis were investigated in Table 3. The bridging oxygens around substitution tetrahedron rise obviously more than normal bridging oxygens, but some shifts lose the balance. These lopsided shifts of bridging oxygens present the torsional deformation of tetrahedron, which was evaluated by variance. The lower variance of $\text{V}[\text{Si}^{\text{IV}}]_2$ site substituting means smaller torsional deformation. On the contrary, the $\text{V}[\text{Si}^{\text{IV}}]_3$ site substituting reflects a strong asymmetry and deformation. In detail, $\text{V}[\text{Si}^{\text{IV}}]_2 < \text{V}[\text{Si}^{\text{IV}}]_1 < \text{V}[\text{Al}^{\text{IV}}] < \text{V}[\text{Si}^{\text{IV}}]_3$, which is consistent with the ordering of substitution energy. Altogether, this already demonstrates that the stability of V substitution is related to the torsional deformation of local geometry. In all, the V prefers to substitute the hexa-coordinated aluminum in muscovite. In other words, we can obtain a high leaching rate of V, as long as the octahedrals are heavily dissociated and liberated. Thus, the effective destruction of the octahedrals may be meaningful research in the future.

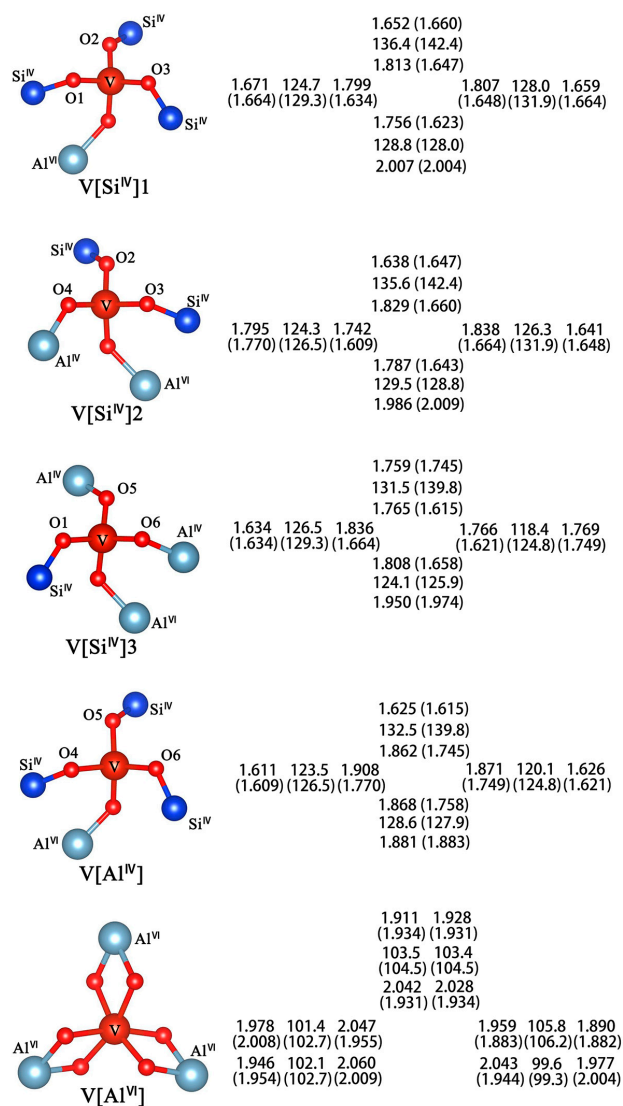


Figure 6. The local bond distances and angles of five configurations after substitution.

Table 3. The shift of bridging oxygens after vanadium substitution (Å).

Site	V[Si ^{IV}]1	V[Si ^{IV}]2	V[Si ^{IV}]3	V[Al ^{IV}]
O1	0.158 *	0.090	0.184 *	0.063
O2	0.152 *	0.189 *	0.077	0.057
O3	0.187 *	0.197 *	0.060	0.056
O4	0.031	0.180 *	0.054	0.115 *
O5	−0.008	0.074	0.102 *	0.157 *
O6	0.081	0.073	0.232 *	0.131 *
(S*) ²	2.34 × 10 ^{−4}	4.82 × 10 ^{−5}	2.88 × 10 ^{−3}	3.00 × 10 ^{−4}

* The shift of bridging oxygens around substitution tetrahedron. The variance formula: $(S^*)^2 = \frac{1}{3} \sum (O_i^* - \overline{O^*})^2$.

3.3. Electronic Properties of Vanadium-Bearing Muscovite

Based on the optimal V-bearing muscovite, it is necessary to further calculate the physical and chemical properties, which can guide either the beneficiation of V-bearing muscovite in the stone coal or the breakage of V–O bond in the lattice.

3.3.1. Density of States (DOS) and Magnetism

The density of states' curves are shown in Figure 7, and the computed magnetic property is also summarized. The muscovite behaves as insulators, with a band gap of 4.83 eV. However, the band gap of muscovite has been verified to be around 5.09 eV [33]. This calculated value is typically underestimated, due to well-known limitations in DFT calculations [34]. A finite density of doping states can be observed at Fermi level in majority spin, which reflects a metallic nature, whereas the Fermi level is located in an energy gap of minority spin states, which suggests that the existence of V does not disturb the insulating property of muscovite in the spin-down channel. Therefore, this material behaves like obvious spin polarization. Furthermore, the partial density of states (PDOS) curves with an energy region of -1 to 4 eV (Figure 8) clearly shows that the $3d$ -state of V overlaps with the $2p$ -state of O at Fermi level, which exhibits the slight p - d hybridization. However, the $3d$ -channel of V contributes to the major states.

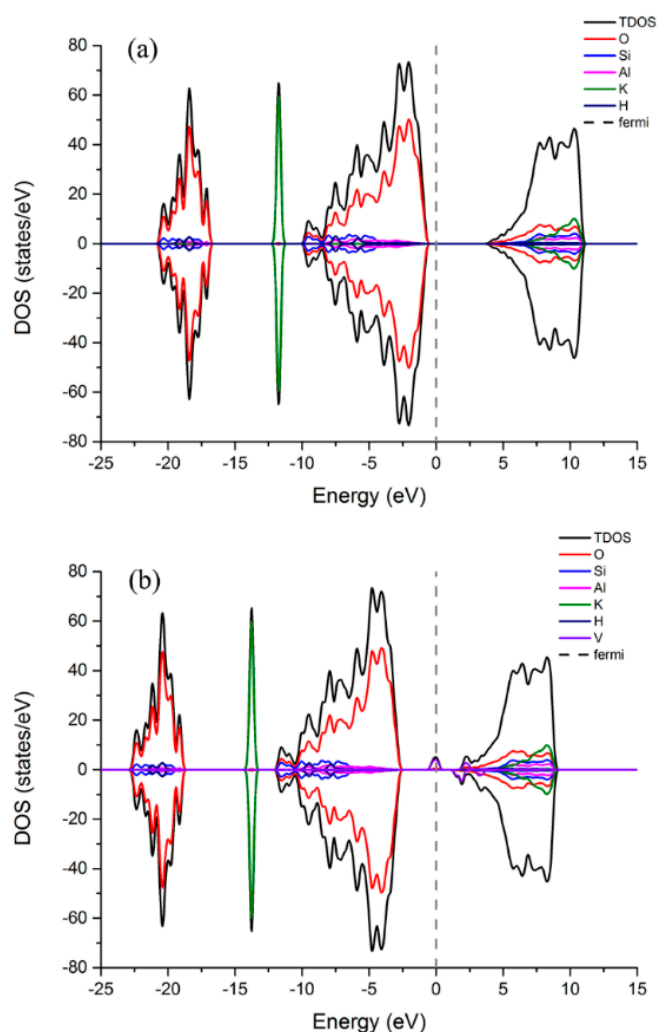


Figure 7. The density of states (DOS) curves of (a) muscovite and (b) muscovite doped with V.

Regarding the magnetic behavior of muscovite, the computed magnetic moment is zero because the total DOS curve for spin up–down contribution is symmetric. Nevertheless, for muscovite containing V, an obvious magnetic moment can be noted, with a value of $1.998 \mu_B$ because the total DOS curve is not symmetrical around the Fermi level. Consequently, the major contribution of magnetism comes from the local magnetic moment of V atoms.

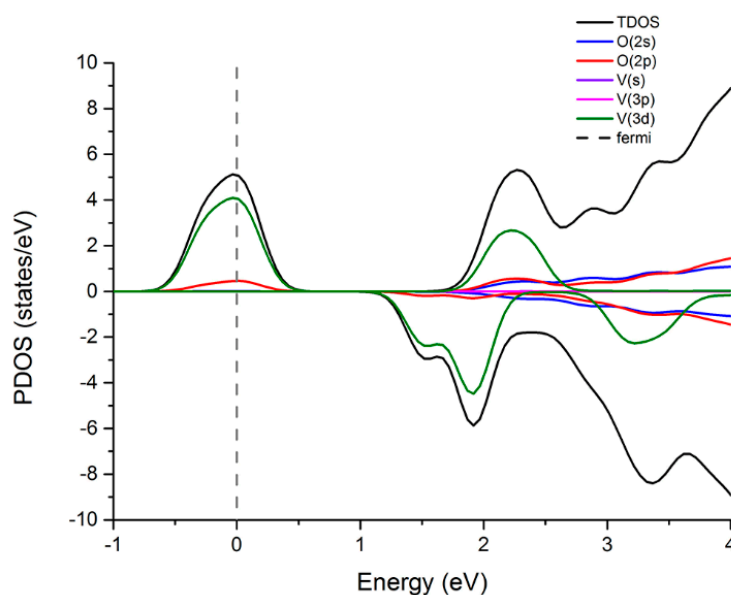


Figure 8. The local partial density of states (PDOS) curves (−1 to 4 eV).

3.3.2. Charge Transfer and Bond Analysis

Local three-dimensional charge density differences with isosurface value of $0.017 \text{ e}/\text{\AA}^3$ of V-bearing muscovite is displayed in Figure 9a, which substantiates the electron transfer. Blue and yellow colors represent losing and gaining electrons, respectively. It is conspicuous that the electrons transfer from V to O. Furthermore, the unique shape of isosurface of V suggests that the p channels of O couple with the d channel of V along with its coordinate axis, consistent with results of PDOS. For intensive study of the characters of V–O bond, we estimated the electron distribution using an electron localization function (ELF) map (Figure 9b). 0–1 represents the localized level of electrons. The (001) plane in the ELF map clearly shows the ionic nature as highly delocalized in the compound. There are localized electrons around V originating from unshielded inner electrons of pseudopotential of V. Therefore, it is responsible for the formation of ionic bonds between V and O. Compared to the covalent bonds, it is easier for ionic bonds to be broken and release V during the leaching process.

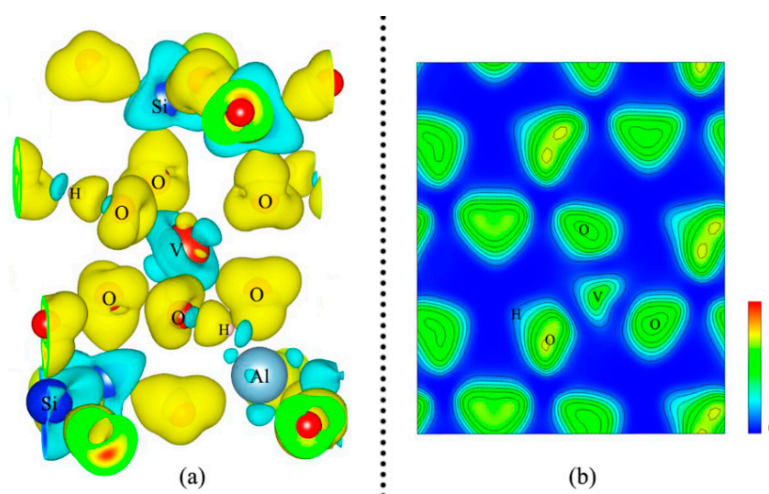


Figure 9. (a) Local three-dimensional charge density difference of V-bearing muscovite; (b) electron localization function map of (001) plane.

4. Conclusions

As the foundation, the optimal muscovite model was tested from the sixteen configurations by periodic DFT theory. After substitution with V, the lattice of muscovite has expanded for a larger ionic radius of V. By employing substitution energy, the Al^{VI} substitution possesses the lower substitution energy. In geometry, the Al^{VI} substitution presents a smaller bond-angle variation than Al^{IV} and Si^{IV}, which further verifies the good plasticity of the Al–O octahedral. In summary, the V prefers to substitute for the hexa-coordinated aluminum more than the tetra-coordinated aluminum or silicon in muscovite. The focus of V extraction shall be concentrated on the effective destruction of octahedrals. Meanwhile, the substitution of V makes this mineral perform narrower band gap and finite magnetism. Combining PDOS with charge transfer, the interaction between V and O atom is based on the *p*–*d* channel hybridization in muscovite. However, the V–O bonds perform an ionic nature for the intense delocalization in the compound. In total, these theoretical data of V-bearing muscovite have been obtained by the quantum chemistry method in detail. It will enhance the theoretical support of V-bearing muscovite and guide the extraction of V from stone coal.

Acknowledgments: This research was financially supported by the National Natural Science Foundation of China (No. 51474162, No. 51404174) and the National Key Science-Technology Support Programs of China (No. 2015BAB18B01).

Author Contributions: Qiushi Zheng and Yimin Zhang conceived and designed the experiments; Qiushi Zheng, Nannan Xue and Qihua Shi performed the calculations and analyzed the data; Yimin Zhang, Tao Liu and Jing Huang contributed servers/softwares/analysis tools; and Qiushi Zheng wrote this paper.

Conflicts of Interest: The authors declare no conflict of interest.

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