Revision 1 DFT simulation of the occurrences and correlation of gold and arsenic in pyrite

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ABSTRACT

Using density functional theory (DFT) calculations, the occurrences and correlation of gold (Au) and arsenic (As) in pyrite were studied, and the effect of As on the structural stability of Au in pyrite (FeS_2) was investigated. The calculated results show that Fe is not likely to be simply substituted with Au under normal circumstances. The presence of As is very conducive to incorporating Au into the pyrite interstitial lattice site along with substitution for the S site. It is predicted that a positive correlation exists between Au and As in pyrite and that the higher is the As concentration, the more easily Au is formed in the pyrite. Additionally, with increasing As content, the Fe site is occupied by the interstitial Au. The pyrite lattice expands with the incorporation of Au and As. Antibonding interactions are found between the Au, Fe and As atoms. The reducibility of pyrite is greatly enhanced due to the presence of Au and As. The electronic structure calculations show that substituting

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Au and As for S atoms does not change the pyrite p-type property and that defect energy levels are present in the conduction band. However, with increasing As concentration, incorporating the interstitial site of Au causes a change from the p-type pyrite to an n-type pyrite, and defect energy levels are mainly located in the energy band gap. The interstitial site of Au causes the pyrite to be spin-polarized at certain As content. In addition, strong interactions are found between Fe 3d and Au 6p orbitals and between Au 5d and As 4p orbitals.

Key words: pyrite; gold-arsenic; correlation; DFT calculation

INTRODUCTION

Gold (Au) and arsenic (As) are two common heterogeneous atoms that often appear together in natural pyrite. It was suggested that a strong association exists between As and Au in pyrite and that a large amount of invisible gold is present in arsenic pyrite. In addition, gold was found to occur more in arsenic-rich pyrite than in arsenic-poor pyrite. Moreover, strong positive correlations between the As and Au content of pyrite were proposed (Wells and Mullens 1973; Cook and Chryssoulis 1990; Arehart et al. 1993; Fleet et al. 1993; Abraitis et al. 2004). Reich et al. (2003, 2005) studied the solubility of gold in arsenic pyrite and suggested a maximum Au/As molar ratio of approximately 0.02.

It was suggested that arsenic could be present at the sulfur site in pyrite, resulting in the formation of the AsS^{3-} dianions within the lattice (Blanchard et al. 2007; Abraitis et al. (2004)), and our study has shown that Au would most likely exist in pyrite incorporated into interstitial lattice sites and substituted for S atoms. Using

XANES measurements on gold-bearing arsenic pyrite, Simon et al. (1999) suggested that the gold present as Au^{1+} was located in the arsenic pyrite lattice. In addition, four-fold-coordinated Au^{1+} was more abundant than two-fold-coordinated forms. However, the nature of four-fold-coordinated Au^{1+} is not well understood. Simon et al. suggested that Au might be present as an Au-As-S compound, where gold would be bonded in four-fold coordination as compared to sulfur and arsenic atoms or in vacancy positions on a cation site in arsenic pyrite. In addition, they suggested that Au^{1+} was most likely incorporated into arsenic pyrite by adsorption onto pyrite surfaces during crystal growth. The coupled substitution mechanism was proposed to explain the strong positive correlation between Au and As in pyrite (Arehart et al. 1993; Fleet et al. 1993). Their studies have clearly shown extensive oscillatory zonation in both the Au and As contents of single pyrite grains. It was suggested that the AsS^{3-} dianion may be charge compensated by Au^{3+} in the mineral lattice, i.e., Au^{3+} substitutes for Fe^{2+} and AsS^{3-} substitutes for the S_2^{2-} dianion. Simon et al. (1999) suggested that the correlation between gold and arsenic might be related to the role of arsenic in enhancing the adsorption of gold on the pyrite surface, possibly through semiconductor effects.

Some studies on the mode of occurrence of gold and arsenic in pyrite have been conducted; however, the crystal structure of pyrite bearing gold and arsenic and whether there is a positive correlation between them are still not very clear. Moreover, the detailed properties of Au- and As-bearing pyrite are not very well studied or understood. In this study, using density functional theory (DFT) calculations, the

66 occurrences and correlation of Au and As in pyrite were studied; additionally, the
67 effect of As on the structural stability of Au in pyrite was investigated.

68 **COMPUTATIONAL DETAILS**

69 Based on density functional theory, all calculations were performed using
70 CASTEP, GGA-PW91 (Perdew et al. 1992). Only the valence electrons Fe $3d^6\,4S^2$, S
71 $3s^2\,3p^4$, As $4s^2\,4p^3$ and Au $5d^{10}\,6s^1$ were considered explicitly through the use of
72 ultrasoft pseudopotentials (Vanderbilt 1990). The effects of the supercell size on the
73 defect properties were investigated, and a 2×2×2 pyrite supercell size ($Fe_{32}S_{64}$) is
74 sufficient to guarantee reliable calculation results. When a plane wave cut-off energy
75 of 270 eV was used, the calculated lattice parameter and band gap were 5.418 Å and
76 0.60 eV, respectively, compared to the experimental values of 5.417 Å (Prince et al.
77 2005) and 0.95 eV (Schlege and Wachter 1976). A Monkhorst-Pack (Monkhorst and
78 Pack 1976; Pack and Monkhorst 1977) *k*-point sampling density of 2×2×2 was used.
79 The convergence tolerances for the geometry optimization calculations were set to a
80 maximum displacement of 0.002 Å, a maximum force of 0.08 $eV\cdot Å^{-1}$, a maximum
81 energy change of 2.0×10^{-5} $eV\cdot atom^{-1}$ and a maximum stress of 0.1 GPa, and the
82 self-consistent field (SCF) convergence tolerance was set to 2.0×10^{-6} $eV\cdot atom^{-1}$. In
83 addition, the spin calculation was performed during the simulation. It was indicated
84 that the calculation will be performed using different wavefunctions for different spins
85 (Hohenberg and Kohn 1964; Kohn and Sham 1965; Barth and Hedin 1972; Vosko et
86 al. 1980; Cocula et al. 2003).

87 The formation energy refers to the energy required for an Au (As) atom to

88 incorporate into the crystal. Here, the formation energy of a site-defect element in the
89 pyrite lattice, ΔE , is defined as follows (Nishidate et al. 2008):

90 $$\Delta E = E_{product}^{total} + E_x - E_{reactant}^{total} - E_{Au(As)}$$

91 where $E_{product}^{total}$ and $E_{reactant}^{total}$ are the total energies of those pyrites bearing As and/or
92 Au and perfect pyrites, respectively. E_x and $E_{Au(As)}$ are defined as the calculated
93 total energies of the substituted matrix atom (x= Fe or S) and the Au or As atom, i.e.,
94 the pseudo atomic energy, which is calculated during the optimized cell process. The
95 smaller is the value of ΔE , the more likely it is that the element exists in pyrite.

96

97 **CORRELATION OF AU AND AS IN PYRITE**

98 Our studies have shown that gold (Au) would most likely exist in the pyrite
99 crystal at the interstitial lattice sites and through substitution for S atoms, and As
100 substituting for S was the most energetically favored mechanism (Savage et al. 2000;
101 Blanchard et al. 2007).. In this study, Au substituting for Fe in pyrite under the effect
102 of As was investigated. This reaction is shown as follows:
103 One Au substituting for one Fe and one As substituting for one S:

104 $$Fe_{32}S_{64} + Au + As \rightarrow Fe_{31}S_{63}AuAs + Fe + S \quad (1)$$

105 Reactions (2)-(4) describe the substitution of Au for S in pyrite with increasing
106 As concentration, and reactions (5)-(9) describe the Au at interstitial sites in pyrite
107 under the As mass concentrations of 0.0%, 1.93%, 3.82%, 5.67% and 7.48%,
108 respectively.
109 One As and one Au substituting for one S_2 unit at the same time:

$$Fe_{32}S_{64} + As + Au \rightarrow Fe_{32}S_{62}AsAu \quad (2)$$

One Au substituting for the S of the AsS unit:

$$Fe_{32}S_{63}As + Au \rightarrow Fe_{32}S_{62}AsAu + S \quad (3)$$

One Au substituting for one As of the As_2 unit:

$$Fe_{32}S_{62}As_2 + Au \rightarrow Fe_{32}S_{62}AsAu + As \quad (4)$$

One Au incorporating into the interstitial site of $Fe_{32}S_{64}$:

$$Fe_{32}S_{64} + Au \rightarrow Fe_{32}S_{64}Au \quad (5)$$

One Au incorporating into the interstitial site of $Fe_{32}S_{64}$ substituted by one As atom:

$$Fe_{32}S_{63}As + Au \rightarrow Fe_{32}S_{63}AsAu \quad (6)$$

One Au incorporating into the interstitial site of $Fe_{32}S_{64}$ substituted by two As atoms:

$$Fe_{32}S_{62}As_2 + Au \rightarrow Fe_{32}S_{62}As_2Au \quad (7)$$

One Au incorporating into the interstitial site of $Fe_{32}S_{64}$ substituted by three As atoms:

$$Fe_{32}S_{61}As_3 + Au \rightarrow Fe_{32}S_{61}As_3Au \quad (8)$$

One Au incorporating into the interstitial site of $Fe_{32}S_{64}$ substituted by four As atoms:

$$Fe_{32}S_{60}As_4 + Au \rightarrow Fe_{32}S_{60}As_4Au \quad (9)$$

The calculated formation energies for reactions (1)-(9) are shown in Table 1. The formation energies of Au substituting for Fe (reaction (1)), Au substituting for S (reaction (2)) and Au incorporating into the interstitial site (reaction (5)) are 10.97, 4.62 and 5.89 eV, respectively. This result suggests that reaction (1) is difficult to undergo, indicating that it is almost impossible for Fe to be substituted simply by Au under normal circumstances. For reactions (2) to (4), the formation energies of Au substituting for S decrease with increasing As concentration. This result indicates that

the reactions are promoted due to the presence of As. In addition, comparing reactions (3) and (4) show that the reaction of Au substituting for As (reaction (4)) is more likely to occur than the reaction of Au substituting for S (reaction (3)), which suggests that the presence of As was conducive to the incorporation of Au. When Au is incorporated at interstitial sites (reactions (5)-(9)), it is shown that the formation energy is significantly lowered from +5.89 eV to +0.67 eV, with an increasing As concentration of 0% to 7.48%, suggesting that the reactions are promoted as the As concentration increased.

The formation energy calculation results show that the presence of As is very conducive to the incorporation of Au into pyrite, regardless of whether the Au is in the S site or interstitial site, and it can be concluded that a positive correlation exists between Au and As in pyrite. In addition, it is noted that the formation energies of reactions (8) and (9) are obviously low compared to other reactions, which suggests that such highly concentrated As bearing structures are very favorable for the incorporation of Au into pyrite.

CRYSTAL STRUCTURE OF PYRITE CONTAINING AU AND AS

Fig. 1 and 2 show the reacting processes of (2)-(9). It can be observed from Fig. 1 that the incorporation of Au and As into the S site has a small influence on the internal structure of the pyrite crystal, and the structures of their surrounding Fe and S atoms are not influenced. This result suggests that the pyrite structure would be stable when Au and As are introduced into S sites.

The pyrite crystal structure with Au at an interstitial site is shown in Fig. 2. It is

154 shown that the structure of pyrite with an interstitial Au at an As concentration of
155 1.93% ($Fe_{32}S_{63}AsAu$) was similar to that of pyrite at an As concentration of 0%
156 ($Fe_{32}S_{64}Au$). However, the pyrite structure is significantly changed with a further
157 increase in the As concentration. It is clearly shown that the Fe1 atom (in the vicinity
158 of Au) in $Fe_{32}S_{62}As_2Au$, $Fe_{32}S_{61}As_3Au$ and $Fe_{32}S_{60}As_4Au$ is repelled into the hole due
159 to the incorporation of Au, and its original position is occupied by Au. These results
160 suggest that Au may exist in pyrite by substituting for Fe at a high As content.

161 The cell lengths and angles of pyrite containing Au and As were investigated, as
162 shown in Table 2. The incorporation of Au and As into S sites ($Fe_{32}S_{62}AuAs$) results
163 in a small pyrite lattice expansion, and the expansion rate is only of 0.34%, while the
164 incorporation of interstitial Au lead to a great deformation of the lattice, and the
165 expansion rate is greater than 1%. In addition, the degree of changes in angles of
166 pyrite cell is different due to the different incorporation behavior of Au. The
167 interstitial Au results in a greater degree of changes in crystal angles than the
168 substituting Au. Moreover, the degree of deformation increases with the increase in As
169 content. This result is related to the covalent radii of the atoms (Au (1.34 Å), As (1.21
170 Å), Fe (1.17 Å) and S (1.02 Å)).

171 The Mulliken overlap population of bonds may be used to assess the bonding and
172 antibonding states between atoms and positive and negative values indicate bonding
173 and antibonding states, respectively (Segall et al. 1996). The calculated results listed
174 in Table 3 show that the Au atoms are bonded to Fe and As atoms and are present in
175 an antibonding state in the pyrite. The bond populations between As-Au and Fe-Au

bonds are stronger in $Fe_{32}S_{62}AsAu$ and $Fe_{32}S_{63}AsAu$ than in $Fe_{32}S_{62}As_2Au$, $Fe_{32}S_{61}As_3Au$ and $Fe_{32}S_{60}As_4Au$, suggesting that the antibonding interactions between atoms in the former are greater than in the latter. In addition, for the case of interstitial Au, the antibonding interaction between the Fe and Au atoms is weakened with increases in the As content, while the antibonding interaction between As and Au is not changed significantly.

By analyzing the atomic charge using the charge equilibration (QEq) method, it is shown that As is positively charged in the pyrite. The positive charges on the Fe atoms are lowered due to the incorporation of As. In addition, the positive charges on the Fe and As atoms decrease with increases in the As concentration. These results suggest that the presence of As could enhance the reducibility of the pyrite. After incorporating Au into the crystal, the positive charges on Fe and As are further reduced as the As concentration increases, and the positive charge on the Au atom itself also decreases. The reducibility of pyrite is apparently greatly enhanced due to the presence of Au and As.

ELECTRONIC STRUCTURES OF PYRITE-BEARING AU AND AS

The electronic structures of pyrite would be significantly influenced due to the incorporation of Au and As. The band structures of perfect and Au- and As-bearing pyrites are shown in Fig. 3 (the zero point of the energy was set at the Fermi level, E_F). The substitution of Au and As for S atoms ($Fe_{32}S_{62}AsAu$) do not change the p-type property of the pyrite, and defect energy levels are present in the conduction band.

198 However, with increasing As concentration, the incorporation of Au at an interstitial
199 site change the p-type pyrite to an n-type pyrite, and defect energy levels are mainly
200 located in the energy band gap. In addition, Fig. 3 shows that Au at the interstitial site
201 causes the pyrite to be spin-polarized (the solid line indicates the spin-up state (alpha),
202 and the dashed line indicates the spin-down state (beta)) at a certain As content. The
203 spin density of states (DOS) is mainly derived from the Fe 3d state, and the magnetic
204 moments are 0.33 hbar.

205 The changes in the electronic structures can be clearly observed from the DOS of
206 the pyrite, as shown in Fig. 4. It is shown that the DOS of $Fe_{32}S_{62}AsAu$ (Au and As
207 substituting for S atoms) is very similar to that of $Fe_{32}S_{64}$, whereas the DOS of
208 $Fe_{32}S_{64-x}As_xAu$ (x=1-4) are significantly shifted to a low-energy value, and there are
209 apparent DOS between the valence band and conduction band. It is noted that there is
210 DOS at the Fermi energy level for pure pyrite ($Fe_{32}S_{64}$) which is insulating material.
211 One of the reasons for this result is that the Fermi energy level is underestimated in
212 the DOS calculation. In addition, the setting of the Gaussian broadening of the
213 eigenvalues (smearing width) is also very important for the calculation.

214 By analyzing the Mulliken bond population, it has been shown that antibonding
215 interactions existed between the Au-Fe atoms and Au-As atoms. This interaction can
216 be further analyzed by plotting the density of states of the atoms, where the
217 antibonding interactions of the s, p and d orbitals between atoms can be clearly shown.
218 Fig. 5 presents the s, p and d orbitals of Au, As and Fe at energies ranging from -2 to 2
219 eV. It can be clearly seen that strong hybridizations occur between the 6p and 5d

220 orbitals of the Au atoms. In addition, strong interactions are found between the Fe 3d
221 and Au 6p orbitals and between the Au 5d and As 4p orbitals.

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Figure captions

FIGURE 1. Reacting processes of (2)-(4). Au is incorporated into the S site under different As mass concentrations.

FIGURE 2. Reacting processes of (5)-(9). Au is incorporated at interstitial site in pyrite under different As mass concentrations.

FIGURE 3. Band structures of perfect and Au- and As-bearing pyrites. The solid line indicates the spin-up (alpha) state, and the dashed line indicates the spin-down (beta) state. The zero of the energy has been set at the Fermi level, E_F.

FIGURE 4. Density of states (DOS) of the perfect pyrite and that of Au- and As-bearing pyrite. The zero of the energy has been set at the Fermi level, E_F.

FIGURE 5. DOS of Fe, Au and As atoms in pyrite. The zero of the energy has been set at the Fermi level, E_F.

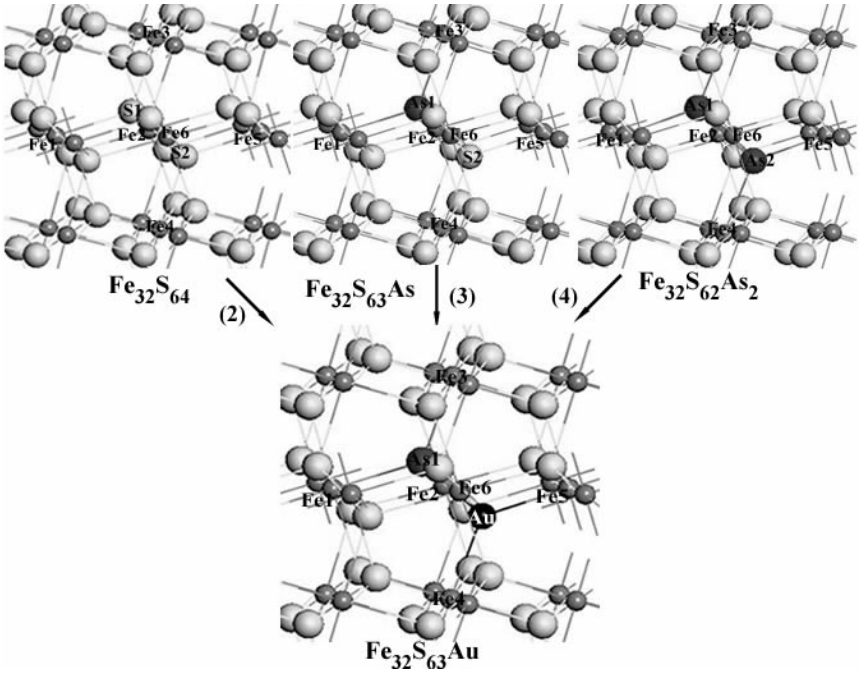

FIGURE 1

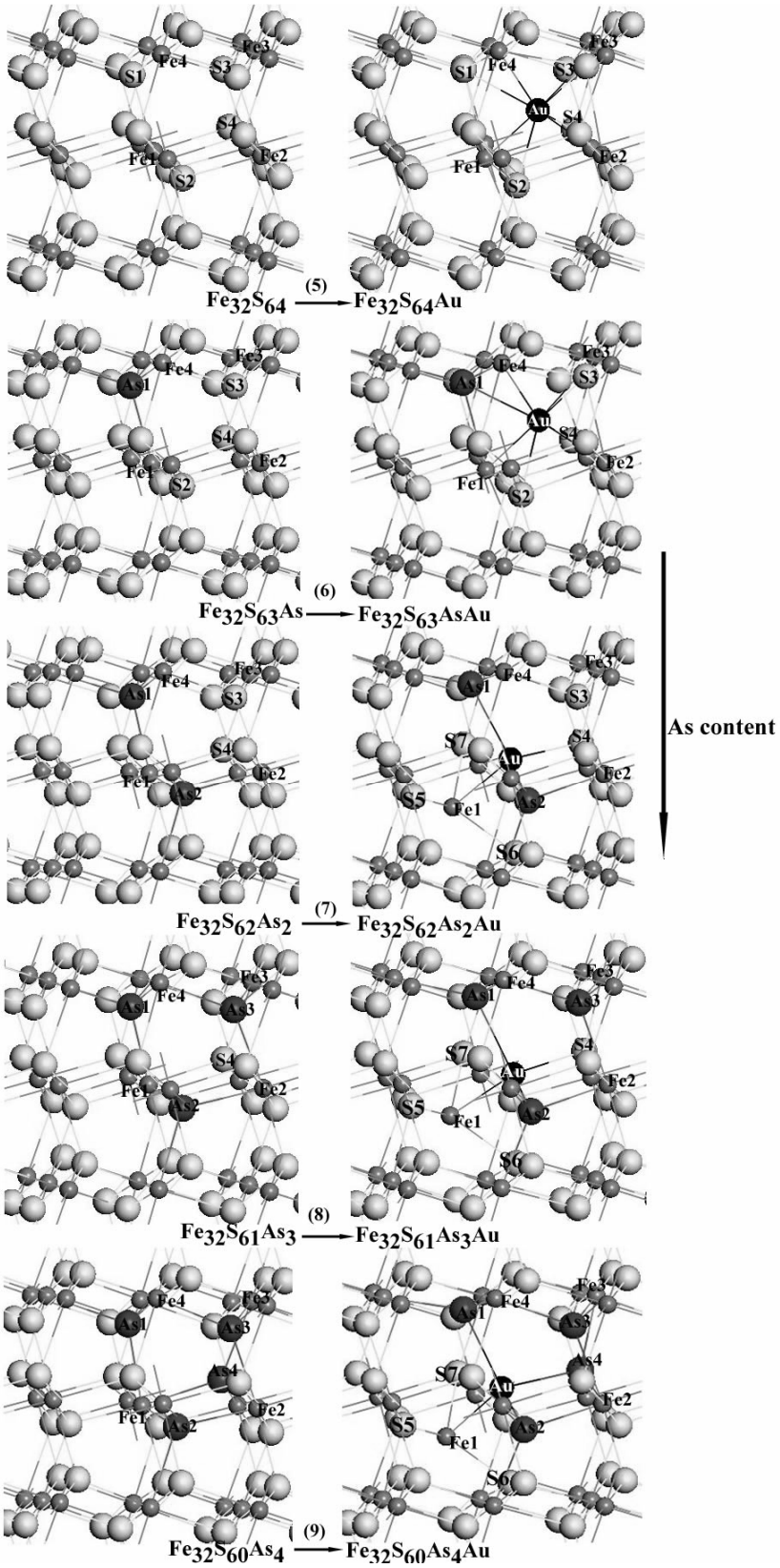
Fe32S64 (5) Fe32S64Au
Fe32S63As (6) Fe32S63AsAu
Fe32S62As2 (7) Fe32S62As2Au
Fe32S61As3 (8) Fe32S61As3Au
Fe32S60As4 (9) Fe32S60As4Au
As content

FIGURE 2

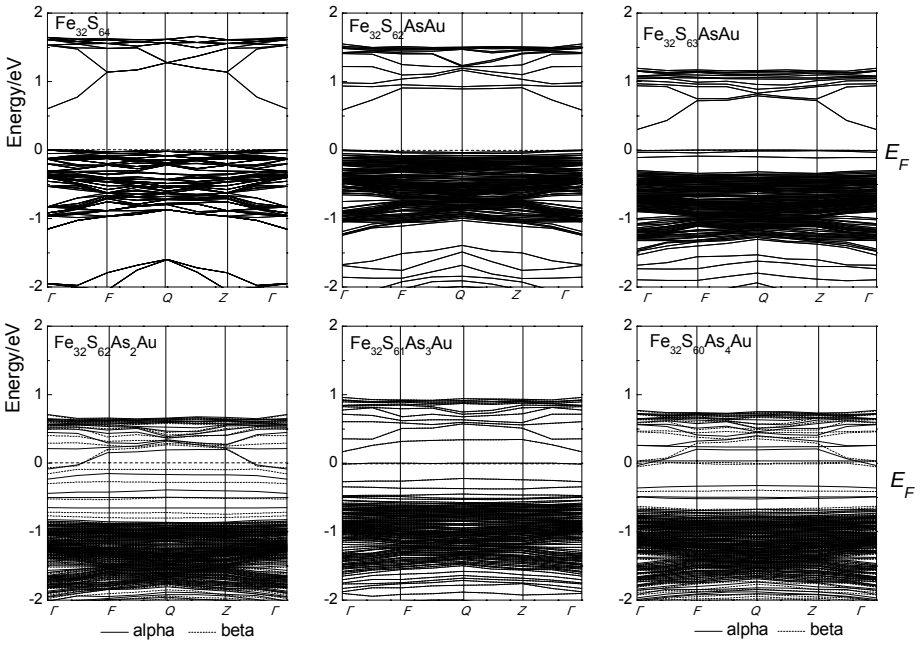

FIGURE 3

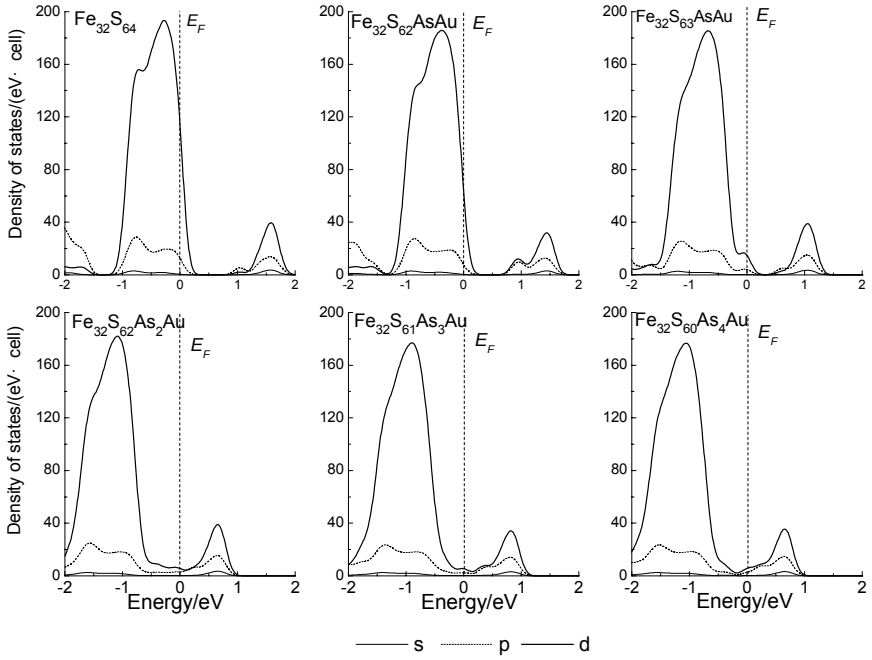

FIGURE 4

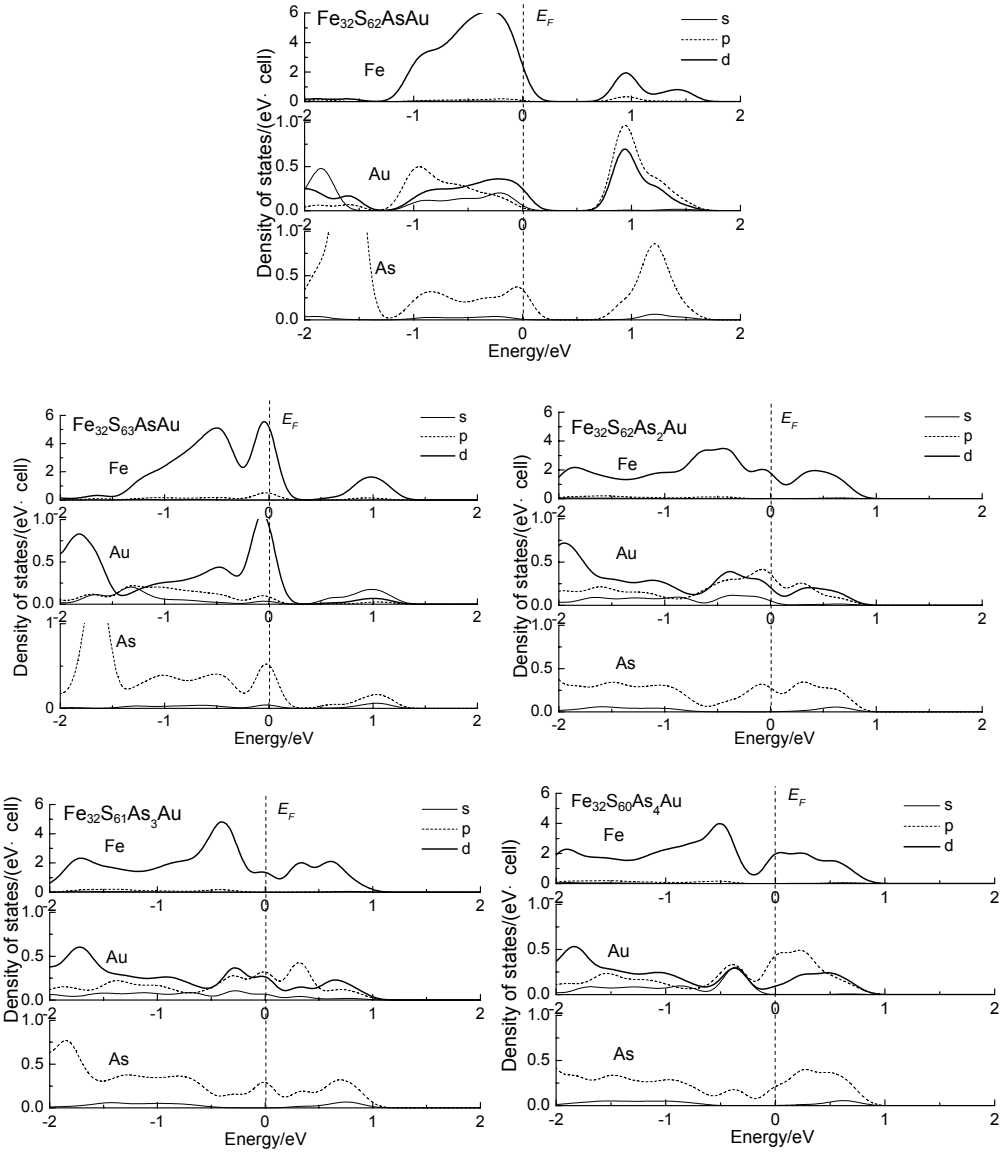
Fe32S62AsAu
Fe32S63AsAu
Fe32S62As2Au
Fe32S61As3Au
Fe32S60As4Au
EF
s
p
d
Fe
Au
As
Density of states/(eV· cell)
Energy/eV

FIGURE 5

TABLE 1 Formation energies for reactions (1)-(9)

Reactions	Formatin energy /
(1)	+10.97
(2)	+4.62
(3)	+3.96
(4)	+2.86
(5)	+5.89
(6)	+4.67
(7)	+2.00
(8)	+1.33
(9)	+0.67

Note: The standard deviation value is 0.005 eV.

TABLE 2 Lattice structure of pyrite containing Au and As

	Cell lengths /Å			Angles /degree		
Species	a	b	c	α	β	γ
$Fe_{32}S_{64}$	10.836	10.836	10.836	90.00	90.00	90.00
$Fe_{32}S_{62}AsAu$	10.873	10.873	10.873	89.84	90.22	89.80
$Fe_{32}S_{63}AsAu$	10.958	10.949	10.955	89.72	89.68	89.86
$Fe_{32}S_{62}As_2Au$	10.979	10.947	10.950	89.73	89.76	89.70
$Fe_{32}S_{61}As_3Au$	10.984	10.945	10.962	89.69	89.83	89.64
$Fe_{32}S_{60}As_4Au$	10.975	10.975	10.972	89.65	89.64	89.67

Note: The standard deviation value for cell length is 0.002 Å and for angle is 0.01 degree.

TABLE 3 Mulliken population of bond in pyrite

	Species	Bond	Length /Å	Population
Substituting Au	$Fe_{32}S_{62}AsAu$	As1-Au	2.426	-0.12
		(Fe4, Fe5, Fe6)-Au	2.425	-0.40
Interstitial Au	$Fe_{32}S_{63}AsAu$	As1-Au	2.381	-1.08
		(Fe1, Fe2, Fe3, Fe4)-Au	2.380—2.666	-0.82—-1.26
	$Fe_{32}S_{62}As_2Au$	(As1, As2)-Au	2.408	-0.05
		Fe1-Au	2.419	-0.30
	$Fe_{32}S_{61}As_3Au$	(As1, As2)-Au	2.428	-0.03
		Fe1-Au	2.408	-0.22
	$Fe_{32}S_{60}As_4Au$	(As1, As2, As4)-Au	2.455	-0.05
		Fe1-Au	2.393	-0.05

Note: The standard deviation value of bond length is 0.002 Å..