Mn substitution and distribution in goethite and influences on its photocatalytic properties: A combined study using first-principles calculations and photocatalytic experiments

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ABSTRACT

Goethite and modified goethites have been found as good photocatalysts because their conduction band can mediate electron transfer in various redox processes. Many kinds of metal elements can be incorporated into the structure of goethite to form solid solutions in nature, but their optoelectronic properties have not been well disclosed. Mn-substituted goethite is one of the potential photocatalysts, which can exhibit high-photocatalytic activity in many Earth's surface processes. Based on the first-principles calculation, pairwise interaction energies and static lattice energies of goethitegroutite solid solution were computed, and the most thermodynamically stable configurations of Mn-substituted goethite were determined. The results indicate that Mn³⁺ ion tends to distribute within the cation layer parallel to the (001) plane. Phase relations of goethite-groutite solid solution were derived by subsequent configurational statistics with energies of all 2^{32} configurations of a $2 \times 1 \times 4$ supercell with 32 exchangeable cations. The phase diagram shows that no more than 3 mol% Fe of goethite can be substituted by Mn ions. Therefore, Mn-substituted goethite is thermodynamically metastable or bears groutite-like clusters/lamellae. Furthermore, the effects of Mn substitutions on the band gap were experimentally and theoretically investigated. It is found that a small amount of Mn-substitution can reduce the band gap of goethite significantly, and the decrease ceases when the Mn content is higher than 3-4 mol%. Such a decrease in band gap causes red-shift to the photo response wavelength of goethite and improves the responding capability. This improvement was confirmed in the experiments of photocatalytic degradation of methylene blue (MB). Such kind of photocatalytic reaction probably can happen widely in natural environments. Therefore, the contribution of photocatalysis of natural goethites to geochemical processes on Earth's surface should be considered.

Keywords: Goethite, Mn substitution, solid solution, band gap, photocatalytic property, firstprinciples calculation

INTRODUCTION

Goethite is one of the most important and common minerals among natural iron oxides and is usually applied to adsorb various toxic anions or heavy metals in environments (Granados-Correa et al. 2011; Mamindy-Pajany et al. 2011; Rahimi et al. 2015). Goethite and modified goethites are good photocatalysts because of their nontoxic nature and natural abundance and have been widely investigated to develop the performance for photocatalytic decomposition of both natural molecules like nucleic acid, aldehydes (Kakuta et al. 2014; Murakami et al. 2011; Shkrob et al. 2011) and artificial organic pollutants such as dyes, aniline, plastic, and so on (Du et al. 2008; Liu et al. 2010, 2011; Zhou et al. 2010). The band gap of pure goethite is 1.6–2.5 eV [wavelength (nm) = 1240/band gap (eV)] due to the particle size (Sherman 2005; Zhang et al. 2011), so it is a visible-light-responsive photocatalyst but does not cover the whole visible spectrum. Many studies revealed that doped goethite shows higher photocatalytic ability than pristine one (Liu et al. 2010, 2011).

Natural goethite can incorporate many di-, tri-, and tetravalent cations (e.g., Mn^{3+} , Ni^{2+} , Al^{3+} , Co^{2+} , Cr^{3+} , Pb^{2+} , etc.) on the Fe sites, and the incorporated ions can modify many properties of goethite such as thermodynamic stability, photocatalytic ability, and adsorption characteristics (Alvarez et al. 2007, 2008, 2015; Carvalho-E-Silva et al. 2003; Kaur et al. 2009; Kusuyama et al. 2002; Liu et al. 2018). Among all the impurity elements, Mn^{3+} is the most similar cation to Fe³⁺ because they have the same valence and similar cation radii (~0.645 Å) (Shannon 1976). Thus, Mn can be readily incorporated into the goethite structure to form goethite-groutite solid solutions, where the Mn-Fe substitution can be up to 15 mol% (Cornell and Giovanoli 1987; Gasser et al. 1999; Scheinost et al. 2001).

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The change in structure caused by Mn substitution in goethite and the distribution of Mn have been studied for decades. Although Mn³⁺ has a very similar cation radius as Fe³⁺, the substitution of Mn into goethite can cause lattice distortion because of the Jahn-Teller effect (Burns 1993). The four equatorial Mn-O bonds in an Mn3+ octahedron shorten and two axial Mn-O bonds elongate, which increases the cell parameter bwhile decreasing a and c (Alvarez et al. 2006, 2007; Liu et al. 2018; Scheinost et al. 2001; Stiers and Schwertmann 1985). In theory, such distortion alters the electronic structure and significantly affects the band gap and photocatalysis ability of goethite. Rout et al. (2014) suggested that the band gap of goethite decreases as the Mn content increases, but they did not reveal the physical mechanism. Although the content of Mn in goethite and related effects have been well documented (Alvarez et al. 2006, 2007, 2015; Manceau et al. 2000; Sileo et al. 2001; Singh et al. 2002; Wu et al. 2007), few studies focused on the distribution of Mn in goethite. By plotting the fraction of Mn vs. the fraction of Fe dissolved during dissolution, the Mn distribution within goethite was considered a homogeneous distribution (Alvarez et al. 2007, 2015). However, other researchers suggested that there were groutite-like clusters or Mn-rich zones in the goethite structure even at low-Mn content (~2.5 mol%), based on experimental data from X-ray diffraction (XRD), X-ray absorption fine structure (XAFS) spectroscopy, and analytical transmission electron microscopy (TEM) (Gasser et al. 1999; Scheinost et al. 2001). The driving force for the cluster formation of groutite may be the incompatibility between increasingly distorted MnO₆ octahedra and the more isotropic host FeO₆ octahedra. Our previous analysis of extended X-ray absorption fine structure (EXAFS) determined the average length of Mn-O and Mn-Fe/Mn bonds, but was not able to determine the presence of Mn cluster (Liu et al. 2018). High-resolution transmission electron microscopy (HR-TEM) seems to be the only experimental technique to recognize the actual distribution of Mn impurity yet still with difficulty.

Molecular simulation methods have become increasingly important in investigating atomic-level properties of minerals and sometimes become promising alternatives to experimental approaches. First-principles methods have been widely applied to calculate specific properties of minerals, such as structure (Chatterjee and Saha-Dasgupta 2010), phase transition (Oganov et al. 2005), adsorption (Zhao et al. 2018), diffusion (Ammann et al. 2010), and isotope fractionation (Huang et al. 2013). In this study, first-principles calculations were employed to investigate the Mn distribution in goethite phases and explain the thermodynamical stability of Mn-substituted goethite from theoretical analysis based on a $2 \times 1 \times 4$ supercell with 32 cations. Several representative configurations were chosen to compute the band structures and the density of state (DOS), which were subsequently applied to yield band gaps. In addition, synthetic Mnsubstituted goethites were prepared and characterized by using XRD, inductively coupled plasma-optical emission spectrometry (ICP-OES) and UV-vis diffuse reflection spectra (DRS). The indirect band gaps of goethite were inferred and then compared to our calculations. Subsequent degradation photocatalytic experiments of MB with pure and Mn-substituted goethites were performed to verify the results of first-principles calculations.

Methods

Computational details

The configurational statistics method with Becker's correction (Becker et al. 2000; Liu et al. 2016) was used to calculate the free energy of mixing and phase relations of (Mn,Fe)OOH solid solution, where the energy of a supercell was computed by employing the cluster expansion method based on a series of pairwise interactions from the double-defect method (Vinograd et al. 2009; Vinograd and Winkler 2010). The details of the method can be found in related references. Here a $2 \times 1 \times 4$ supercell was utilized with 32 cations based on a unit cell with the Pbnm space group (Nagai et al. 2003). For each end-member, one single-defect structure and 17 double-defect structures together with the pure end-member were selected to calculate the pairwise interactions. These 17 kinds of paired defects were placed in the supercell with the distance range of 3.0-8.3 Å to keep every configuration symmetrically independent. The size of the supercell was selected such that the pairwise interaction of the defect pair vanishes to zero as the distance increases. The static energies of all these configurations were calculated with density functional theory and an on-site Coulomb repulsion parameter U (DFT+U) in the PBE type gradient generalized approximation (GGA) (Perdew et al. 1996) using the projector augmented-wave method (PAW) (Blöchl 1994) integrated into the Vienna ab initio simulation package (VASP), version 5.4.4 (Kresse and Furthmüller 1996; Kresse and Joubert 1999). The effective U values are 3.9 and 5 for Mn and Fe, respectively, which were utilized in some previous studies on electronic properties of Fe/Mn oxides or oxyhydroxides successfully (Alexandrov and Rosso 2015; Lee et al. 2020; Jain et al. 2011; Otte et al. 2012). The cutoff energy for the planewave basis set was 520 eV and the spin-polarized method was used. The k-space was sampled by the Monkhorst-Pack method to keep the actual spacing density at about 0.03 Å⁻¹. The pairwise interactions, viz. Js, were calculated from the excess energies of these configurations, which were calculated by subtracting the mechanical mixing energies of the two end-members from the static energies. All these Js were consequently applied to calculate the energies of all the 232 configurations of different compositions of (Mn,Fe)OOH solid solution in a $2 \times 1 \times 4$ supercell by employing the cluster expansion method. Then the isotherms of free energy of mixing can be calculated by thermodynamic statistics, which can be used to construct phase relations of (Mn,Fe)OOH solid solution by common tangent analysis (Liu et al. 2016).

To investigate the optoelectronic effect of the Mn substitution, several special structures (several structures with minimum energy, maximum energy, and random structure for different compositions due to the static lattice energy calculations) were selected in a $2 \times 1 \times 4$ supercell and a $2 \times 1 \times 3$ supercell, and then their band structures and DOS were calculated with the similar parameter setting except the k-space sampling. A much denser k-space sampling was applied to the DOS calculation, and a certain path in the Brillouin zone was selected in the calculations of band structures. The band gap was consequently analyzed from the band structures and DOS.

Experimental details

Preparation of goethite and Mn-substituted goethite. The Mn-substituted goethites were synthesized according to a reported method (Alvarez et al. 2007; Liu et al. 2018). Briefly, 25 mL 1 mol/L Fe(NO₃)₂ and x (the x = 0, 1, 2.5, 5) mL 0.5 mol/L Mn(NO₃)₂ were mixed, thereafter 45 mL 5 mol/L KOH solution into the mixture was added with stirring. After adding the KOH solution, DI water was added to reach a concentration of 0.3 mol/L KOH. The suspensions were aged at 60 °C for two weeks, then centrifuged and washed with DI water several times. The collected solids were re-suspended in dilute HCI to remove poorly crystallized materials before being washed with DI water again and air-dried.

Characterization of synthesized goethite samples. The mineral phases of the collected solids were characterized by XRD analysis with a Bruker D8 Advance Diffractometer using CuKa radiation (0.02° per step). The Mn and Fe contents in goethite samples were measured using an inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkinElmer, San Diego, California) with a relative standard deviation of $\leq 2\%$ after completely dissolving in a 6 mol/L HCl solution at 80 °C. UV-vis DRS of the samples were collected using a DUV-3700 spectrophotometer from 200 to 1000 nm, and BaSO₄ was used as the reference material. The indirect band gap was calculated using the equation of $(ahv)^2 = A(hv-E_g)$, where α is the absorption coefficient, hv is the photon energy, A is a constant, and E_g is the band gap (Chernyshova et al. 2010). The indirect band gap was compared with the results from the first-principles calculations.

Photodegradation of MB by goethite samples. The photocatalytic properties of pure goethite and Mn-substituted goethite were evaluated by measuring their effectiveness for MB degradation in an aqueous solution under visible light (400-780 nm) and infrared light (>800 nm). 20.0 mg of the photocatalyst was dispersed in the 20.0 mL of 10.0 mg/L MB aqueous solution in a 20 mL glass bottle, and then 1.5 mL of hydrogen peroxide (30%, w/w) was added to the suspension using a rolling Incubator (QB-328, Kylin-Bell Lab Instruments) with 30 rpm/min. The system was placed in a dark room for 2 h to reach the adsorption-desorption equilibrium condition. Then the glass bottle was illuminated by a 300 W xenon arc lamp (CEL-HXF300, AULTT). A 400 nm filter (exit spectrum 400-780 nm) was added to limit the spectrum within the visible light range, and an 800 nm filter (exit spectrum >800 nm) was added to limit the spectrum in the infrared light range. The degradation experiment was also operated in a totally dark situation as a control. 1 mL of the mixed solution was transferred from the bottle every 1 h and centrifuged for 10 min at 8854.56 × g. The supernatant was taken out to a semimicro-cuvette (Fisher Scientific) and measured on a UV-vis spectrophotometer (UV3200, MAPADA) at a scan step of 1 nm within the wavelength range of 800-200 nm. For comparison, the degradation of MB with only one of hydrogen peroxide, pure goethite, and Mn-substituted goethite, were also evaluated in visible light, infrared light, and dark condition, respectively. The production of free radical of goethites induced by light was investigated by electron paramagnetic resonance spectroscopy (EPR), and the experimental details were supplied in the Online Materials1 data file.

RESULTS AND DISCUSSION

Pairwise interaction energies in Mn-goethite

Pairwise interaction energies (Js) reflect the change in the interaction energy between a guest cation and a host cation as the distance changes. Ideal Js should converge to zero because the interaction between the defect pair should decrease with the increase in distance, so that they are applicable for calculating thermodynamic properties using a much larger supercell (Becker et al. 2000; Vinograd et al. 2007, 2009). Table 1 and Figure 1 show the computed Js, which converge well with the increase in distance. Online Materials1 Figure S1 shows all the 17 kinds of crystal models used in calculating pairwise interaction energies. It is obvious that the energies calculated with the cluster expansion method are consistent with those calculated directly with VASP (Fig. 2), which shows a good performance of Js. Usually, the first several Js have relatively large absolute values and make the most contribution to the energy difference between different configurations. In this system, the first three Js are the most important ones with the distances of 3.01, 3.29, and 3.43 Å, respectively, which represent the interactions between one impurity cation and the nearest neighbor cation in the [001] direction connected by two bridge O atoms (J_1 in Online Materials¹ Fig. S2), between one impurity cation and the nearest neighbor cation within (001)

TABLE 1	• Pa	airwise	interactio	on energi	es (Js	i) of l	Mn-goethite
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n	Distances	Layers (100) across	$J_{\rm Mn-Mn\ in\ FeOOH}$	J _{Fe-Fe} in MnOOH
	(Å)	by defect pairs ^a	(kJ/mol)	(kJ/mol)
1	3.01	1	-2.4654	-0.6153
2	3.29	0	7.7676	5.7979
3	3.43	0	5.0776	3.0528
4	4.58	0	0.5255	0.5474
5	5.27	0	-0.5398	-0.0077
6	5.29	0	-0.5431	-0.0671
7	5.38	1	1.5820	1.3229
8	5.47	1	0.5430	0.6643
9	5.48	1	0.0574	0.2114
10	5.66	0	-0.6076	-0.9283
11	6.03	2	-1.0676	-0.6651
12	6.09	1	0.2665	0.2085
13	6.41	1	0.9125	0.5646
14	6.77	1	0.0608	0.4828
15	7.57	2	0.1323	0.0928
16	8.02	2	-0.0791	0.0360
17	8.27	2	0.1401	0.3194
			11(1.0.0)	

^a The third column indicates how many layers ||(100) across by defect pairs.



FIGURE 1. Pairwise interactions in Mn-goethite calculated from the excess energies of the single- and double-defect structures. (Color online.)

plane connected by two bridge O atoms (J_2 in Online Materials¹ Fig. S2), between one impurity cation and the nearest neighbor cation within (001) plane connected by one bridge O atom (J_3 in Online Materials¹ Fig. S2). Usually, a positive J value means that the impurity cations with the corresponding distance make a negative contribution to the enthalpy, and vice versa. Thus, the distribution of the impurity cation of the most stable and unstable configurations should obey this rule.

Most thermodynamically stable and unstable configurations

The principle of minimum energy tells that the most stable configuration has the lowest energy (Wang et al. 2011). For the composition of $Mn_{2/32}Fe_{30/32}OOH$ based on a 2 × 1 × 4 supercell, the defect-defect distance of the two most stable structures (Figs. 3a and 3b), and the most unstable structures (Fig. 3c) are 3.29, 3.43, and 3.01 Å, respectively. It is evident that these three structures are exactly corresponding to the first three *Js*. The two stable structures reflect the negative contribution to enthalpy



FIGURE 2. Comparison of the excess energies calculated from VASP and the cluster expansion method for all the symmetrically independent configurations for compositions $Mn_{2/32}Fe_{30/32}OOH$ and $Mn_{3/32}Fe_{29/32}OOH$ based on a 2 × 1 × 4 supercell. (Color online.)



FIGURE 3. The most stable configuration (**a**), the second most stable configuration (**b**), and the most unstable configuration (**c**) for $Mn_{2/32}Fe_{30/32}OOH$ based on a 2 × 1 × 4 supercell. (**d**) Ball and stick model for MnO₆ octahedron from configuration (**a**) and bond lengths. The red and white balls are oxygen and hydrogen, and the purple ball represents Mn. FeO₆ and MnO₆ octahedra are marked with brown and purple, respectively. The dash lines are hydrogen bonds. (Color online.)

from the distribution of the impurities with intervals of 3.29 Å, 3.43 Å within the same layer approximately parallel to the (001) plane, while the unstable structure reflects the positive contribution to enthalpy from the distribution of the impurities with interval 3.01 Å across 1 layer approximately parallel to (001) plane. Based on the above analysis, the impurities distributed within the cation layer approximately parallel to the (001) plane can produce more stable structures. For instance, the four most stable structures for the composition of Mn3/32Fe29/32OOH based on a $2 \times 1 \times 4$ supercell are shown in Figure 4. In fact, besides the configuration with two defect pairs with an interval of 3.29 Å (Fig. 4c), the other three configurations include two defect pairs with an interval of 3.29 and 3.43 Å. All these defect pairs can yield conspicuous negative contributions to the lattice energy of the supercell, which makes these structures most stable with the lowest energies.

Table 2 lists the cell parameters of synthesized and calculated pure goethite and Mn-substituted goethite. Cell parameters a, b, and c were refined with Rietveld Program Topas 6.0. The biggest deviation between calculated parameters and those from XRD analysis (Fig. 5) of synthesized minerals is no more than 1.5%, which shows the good performance of DFT calculations. The variations of cell parameters a, b, and c with the content of Mn in goethite are plotted in Figure 6. It shows that a decreases strongly and c decreases slightly when the content of Mn increases while b increases strongly, and all the trends are approximately linear, i.e., in accord with Vegard's Law (West 1984). One of our previous experimental studies also confirmed such tendencies (Liu et al. 2018). The changes are caused by the Jahn-Teller effect of the MnO_6 octahedron with four shortened equatorial Mn-O bonds (approximately parallel to the *a*-*c* plane) and two elongated axial Mn-O bonds (approximately parallel to *b* axis) (Alvarez et al. 2006, 2007; Scheinost et al. 2001; Stiers and Schwertmann 1985). Indeed, the two axial Mn-O bonds (2.24 and 2.15 Å) are significantly longer than the other four (1.96–2.06 Å) (Fig. 3d). By contrast, the corresponding parameters do not exhibit large variations in pure goethite (2.00 Å for Fe-O(H) bond and 2.11 Å for Fe-O bond).

Gibbs free energy and phase relations of goethite-groutite solid solution

Isotherms of Gibbs free energy of mixing can be computed with configurational statistics based on the energies of all the possible configurations calculated with the cluster expansion method, and here we introduced the entropy correction after Becker et al. (2000). The free energies are positive for all compositions when the temperature is below 423 K (Fig. 7). For the Mn-rich end-member, the free energy becomes negative when the temperature is higher than 423 K, but for the Fe rich end-member, it starts from 523 K. The isotherms are slightly asymmetric, which implies the incorporation of a Fe cation into groutite is easier and costs less energy than a Mn cation into goethite. Although the ion radii of Fe³⁺ and Mn³⁺ are nearly equal, because of the Jahn-Teller distortion in the Mn3+ octahedron, the volume of Mn³⁺ octahedron is slightly larger than that of Fe³⁺. It makes sense that a small cation is easier to substitute into a site occupied by a larger cation than a reverse process. As there is a phase transition from goethite to hematite at about 573 K (Christensen et al. 2007; Gialanella et al. 2010), isotherms of higher temperatures than 573 K seem meaningless. Although



FIGURE 4. The four most thermodynamically stable configurations for $Mn_{3/32}Fe_{29/32}OOH$ based on a 2 × 1 × 4 supercell. The lattice energy increases from **a** to **d**. (Color online.)

12.30

0112 × 1 ×	4 supercens		
Mn content (mol %)	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)
	DFT+U calcu	lations	
0	9.276	10.062	12.268
0.031	9.271	10.087	12.249
0.063	9.270	10.108	12.233
0.094	9.266	10.124	12.219
	Experime	ents	
0	9.219	9.948	12.087
0.018	9.208	9.950	12.078
0.046	9.196	9.955	12.070
0.095	9.183	9.972	12.052

TABLE 2. Cell parameters of goethite with the content of Mn fromDFT+U calculations and experiments, all the data are basedon $2 \times 1 \times 4$ supercells

these isotherms remain meaningless at low pressures, they are meaningful at higher pressures because high pressures bring higher phase transition temperatures for goethite (Majzlan et al. 2003). Because the influence of pressure on free energy is very small (Jung and Schmidt 2011; Jung et al. 2010), the isotherms hardly change in a wide pressure range. Thus, these isotherms are still applicable for the calculation of phase relations.

Generally, negative free energy reflects stability or metastability. The positive values for the compositions near the goethite end-member at room temperature, therefore, imply that they are unstable. On the one hand, considering that the absolute value is very small and some other effects, such as vibrational entropy and pV term in free energy, are neglected in our calculation, the actual value for these compositions may still be negative. Many studies suggest that vibrational entropy can be neglected for such a system because it contributes only no more than 1% to the free energy (Benny et al. 2009; Liu et al. 2015; Ruiz-Hernandez et al. 2010; Wang et al. 2011). Due to the very little deviation of volume from the mechanical mixing of the two end-members in a wide range of pressures, the pV term is very small and can also be neglected. On the other hand, the natural and synthetic substituted goethite with high-Mn contents may be metastable if no groutite cluster is formed, just because there is a high-energy barrier for the transition to stable phases. Hence, the calculated results are not exactly inconsistent with experiments, especially for these very low absolute values of free energy.

The temperature-composition phase relation can be derived from the isotherms of Gibbs free energy of mixing with common



FIGURE 6. Variations of cell parameters (*a*, *b*, and *c*) of goethite with the content of Mn from DFT+U calculations. All the data are based on $2 \times 1 \times 4$ supercells.

Mole fraction of MnOOH

tangent analysis (Fig. 8). The zone below the solvus is unstable or metastable, and the remaining is the stable zone. The phase diagram shows that only a low concentration of Mn impurity (<3 mol%) can be thermodynamically stable in goethite. Therefore, samples with higher Mn impurity may be metastable, or the extra Mn may occur as nanoscale Mn-rich lamellae or clusters in the goethite structure. Gasser et al. (1999) reported Mn-rich zones in Mn-goethites from line scan of X_{Mn} based on transmission electron microscopy (TEM) observation and energy-dispersive X-ray (EDX) analysis. The needle cores of goethite generally had a significantly higher X_{Mn} than the tips. Scheinost et al. (2001) also found groutite-like clusters in Mn-goethites when $X_{\rm Mn}$ is higher than 0.13. According to the analysis of most stable configurations, we deduce that Mn cations prefer to distribute within the cation layer approximately parallel to the (001) plane and form Mn-rich lamellae or clusters.

Several studies suggest the existence of nanoscale lamellae or nanoparticles of impurity during the formation of various solid



FIGURE 5. XRD patterns for pure goethite and Mn-substituted goethite.



FIGURE 7. Isotherms of Gibbs free energy of mixing as a function of mole fraction of MnOOH from 273 to 1073 K with an interval of 25 K.



FIGURE 8. Phase relations of $Mn_xFe_{1,x}$ OOH solid solution derived from isotherms of Gibbs free energy of mixing with common tangent analysis.

solutions (Ciobanu et al. 2011; Gasser et al. 1999; Scheinost et al. 2001; Wu et al. 2019). Because isostructural solid solutions have similar cell parameters, XRD cannot exactly distinguish the intergrowth between two end-members. Such heterogeneous phenomena can only be visualized by a few technological means, for instance, HR-TEM, atomic probe tomography (APT), and other atomic analysis techniques. Hence, the high content of impurities in the mineral should be handled cautiously. Thus, revealing the structure of a solid solution mineral at the atomic level is necessary because mineral properties can be significantly changed by impurity, i.e., "properties depend on structure."

Band structures and DOS

Band structure and DOS of pure goethite and a series of Mnsubstituted goethite (several structures with minimum energy, maximum energy, and random structure for different compositions) were calculated in detail by using the DFT+U method, and band gaps were discerned subsequently. Figure 9 shows the dispersion relations of the electronic structure and related DOS plots for pure goethite and single-Mn-substituted goethite. The unfolding band structure of Mn-substituted goethite calculated based on $2 \times 1 \times 4$ supercell is shown to be compared with that of pure goethite using the method provided by Popescu and Zunger (2012). The bands caused by Mn impurity are very clear in Figure 9b. It is obvious that the DOS plots are asymmetric for up and down electrons because the spin-polarized DFT calculations were executed. The valence band and conduction band can both be divided into two parts, spiculate lower part and relatively flat upper part (Fig. 9). The spiculate lower part contains mainly 3d state electrons of Fe, and the relatively flat upper part contains mainly 2p state electrons of O, while the contribution from 1s state electron of H is quite small. The band gap of pure goethite is 1.87 eV (Fig. 9a). In the single-Mn-substituted goethite, the substituted Mn brings two impurity peaks (mainly containing 3d state electrons of Mn and 2p state electrons of O) between the valence band and conduction band of goethite, which can decrease the band gap significantly by about 0.8 eV (Fig. 9b). The other structures with more Mn impurity can also decrease

by similar values, and the final indirect band gaps are shown in Figure 10. It is reasonable to believe that the band gap of actual Mn-substituted goethite should be within the envelope area outlined by all the calculated results. Note that there is a sharp decrease when the content of Mn is lower than 3 mol%, then it turns out to be a very slow decrease with the increase of Mn content. Such a decrease in band gap will bring the photo response wavelength of goethite from visible light to near-infrared light, i.e., redshift happens. Thus, the existence of the impurity can reduce the band gap and extend the photo response coverage from partial visible light to whole visible light and near-infrared light.

Comparison with measured band gaps of Mn-goethite samples

To verify the DFT calculation results, a series of Mnsubstituted goethites and pure goethite were synthesized and characterized. The XRD patterns show that all the synthetic



FIGURE 9. The dispersion relations of the electronic structure and related DOS of pure goethite (**a**) and single-Mn-substituted goethite (**b**). Although all the selected configurations (black points in Fig. 10) were calculated, the DOS plots are quite similar for goethite with different concentrations of Mn, so only the DOS of single-Mn-substituted goethite is shown here. Orange lines in dispersion relations indicate lower spin bands and cyan lines indicate upper bands. (Color online.)



FIGURE 10. Calculated band gaps based on DFT and experimental band gaps based on UV-vis DRS for different compositions of the solid solution. (Color online.)

samples are goethite (Fig. 5). The Mn contents are 1.8, 4.6, and 9.5% mole fractions determined using ICP-OES after completely dissolving in a 6 mol/L HCl solution. Then UV-vis DRSs of pure and Mn-goethites were collected (Fig. 11a). Usually, the UV-vis DRSs should be converted to Tauc-Mott (TM) plots to disclose the indirect band gap of semiconductor material (Chernyshova et al. 2010). Figure 11b shows the TM plots of pure and Mn-substituted goethites with Ahv/2 against hv, where A represents the UV-vis absorbance and hv the photon energy. The intercept on hv axis from the extrapolation of the linear section of the Tauc-Mott plot defines the indirect band gap. It is observed that the measured band gaps also decrease with the increase of mole fraction of MnOOH and deviate only slightly from the DFT calculated area (Fig. 10). The band gap of pure goethite is 1.84 eV by experiment, which is in accordance with a previous study (Zhang et al. 2011). The decreasing tendency of the band gap with the increase of Mn content agrees with our simulations but with a decrease of about 1 eV. The turning Mn

content is about 4 mol%, comparable with the 3 mol% Mn of our simulation. Considering many approximations have been employed in our DFT calculations, the calculated results are quite close to those of the experiment. As there is a transition Mn content controlling the decrease of the band gap, it indicates that a structure change happens. Meanwhile, the relative flat tendency after the turning point also illustrates a new electron structure in the lattice. Combining previous and our results, we infer that Mn-rich clusters or lamellae can emerge in the goethite lattice even when the content of Mn is slightly higher than 3–4 mol%.

MB photocatalytic degradation of goethite

Both simulation and experimental studies indicate that Mn substitution can bring a significant decrease in the band gap of goethite, which should extend the photo response coverage of goethite to near-infrared light. Thus, a series of reactant combinations for the MB degradation in a dark situation, visible light (400-780 nm), and infrared light (>800 nm) were tested. The MB absorption equilibrium was achieved after 2 h of dark reaction to eliminate the absorption effect of goethite. The results plotted in Figure 12 show the residual MB concentration as a function of reaction time. As a semiconductor mineral, goethite can produce hydroxyl radicals as the main effective oxidizing agent to degrade organic pollutants on its surface with irradiation, and the incorporation of goethite and hydrogen peroxide increases the efficiency of the generation of hydroxyl radicals (Mameri et al. 2016; Ravina et al. 2002). Figure 12a indicates that the catalytic reaction was weak under dark condition compared to Figures 12b and 12c where photocatalytic degradation happened. After 5 h of illumination of visible light, both pure goethite and Mnsubstituted goethite show the photodegradation ability of MB (Fig. 12b), but in the infrared light situation, only Mn-substituted goethite shows obvious photodegradation ability of MB with higher efficiency than in visible light (Fig. 12c). The band gap of pure goethite is 1.84 eV (674 nm) from the experiment, which means photogenerated hydroxyl radicals can be released easily at the surface of minerals. This may explain why photocatalytic degradation can happen easily in visible light but cannot in



FIGURE 11. (a) UV-vis DRS of pure goethite and Mn-substituted goethite; (b) Tauc-Mott plots of UV-vis DRS of pure goethite and Mn-substituted goethite. (Color online.)



FIGURE 12. Plotted MB concentration as a function of reaction time for a series of reactant combinations in (**a**) a dark situation, (**b**) visible light (400–780 nm), and (**c**) infrared light (>800 nm). The first 2 h are for adsorption–desorption equilibrium in **b** and **c**. (Color online.)

infrared light. Both experiment and DFT calculations indicate the incorporation of Mn into goethite brings $a \sim 1 \text{ eV}$ decrease of the band gap, resulting in the release of photogenerated hydroxyl radicals under infrared light.

Electron paramagnetic resonance (EPR) experiments also show Mn-substituted goethite can produce a lot of •OH radicals, but pure goethite can hardly produce radicals under infrared light (Online Materials¹ Fig. S3). It again confirms that Mnsubstituted goethite can generate photoinduced electrons and holes but pure goethite cannot under infrared light. As a result, Mn-substituted goethite has photo response ability in infrared light, while pure goethite does not. Besides, from our previous FE-SEM work (Liu et al. 2018) and the study of Alvarez et al. (2015), the morphology of goethite was not significantly changed by Mn substitution. Both the pure goethite and Mn substituted goethite exhibit acicular shape with similar average length/width (L/W) ratio and no facet change. Thus there is also no evidence for the facet-dependent effect in the photocatalytic degradation process.

In conclusion, the photocatalytic degradation experiments of MB confirm that Mn-substituted goethite has photo response ability not only in visible light but also in infrared light, which means Mn substitution indeed improves the photo response ability of goethite. As goethite widely exists on the Earth's surface, such kind of enhancement of photocatalytic ability probably affects many surface geochemical processes and subsequently affects element cycling.

IMPLICATIONS

As the most stable and common phase of iron oxides in nature, goethite has a strong adsorption capacity for various toxic cations and anions, which has been successfully applied in environmental restoration (Asta et al. 2009; Giménez et al. 2007). The Mn substitution can evidently affect the structural characteristics and surface properties of goethite and enhance its adsorption ability. As the Mn distribution in goethite determines its physical-chemical properties, this study provides one simulation frame and reveals the distribution pattern of Mn impurities in goethite, i.e., the Mn cations prefer to distribute within the cation layer approximately parallel to the (001) plane. We also predict that there may be Mn-rich nanoscale clusters or lamellae in Mn-substituted goethite even with as low-Mn content as 3–4 mol% based on the phase diagram and band gap analysis.

Goethite is a semiconducting mineral on the Earth's and Mars's surface (Klingelhöfer et al. 2005) as its band gap is about 1.6-2.5 eV (Sherman 2005; Zhang et al. 2011), and 1.84 eV from this study, which makes it an active material in photocatalytic processes activated by UV and partial visible light. The incorporation of impurity ions can significantly decrease the band gap of goethite because of the involvement of impurity bands, where Mn substitution enlarges the potential photocatalytic range of goethite to the whole visible and partial near-infrared light. Because visible light is the main solar radiation reaching the Earth, the enlargement of the photocatalytic range provides more solar energy for photocatalysis. Besides, it still has photocatalytic ability while the visible light is blocked or insufficient in some special environments, not only on the Earth but also on some other terrestrial planets like Mars. Doped goethite may be involved in various photochemical processes, for instance, solar-induced generation of reactive oxygen species (ROS) (Nguyen et al. 2018). ROS values can initiate subsequent degradation of organic compounds, which may be one possible reason to explain the abiotic oxidation of organic compounds in the desert on Earth and the absence of organics on Mars (Georgiou et al. 2015; Schuttlefield et al. 2011). In summary, not only goethite but also some other semiconductor minerals can be modified by impurities under complex hypergenic environments, which may bring obvious changes in photocatalytic properties (Li et al. 2018). Such photocatalytic ability can probably affect the element cycling to a non-negligible extent on both early and modern terrestrial planets.

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References cited

- Alexandrov, V. and Rosso, K.M. (2015) Ab initio modeling of Fe(II) adsorption and interfacial electron transfer at goethite (α-FeOOH) surfaces. Physical Chemistry Chemical Physics, 17, 14518–14531, https://doi.org/10.1039/C5CP00921A.
- Alvarez, M., Rueda, E.H., and Sileo, E.E. (2006) Structural characterization and chemical reactivity of synthetic Mn-goethites and hematites. Chemical Geology, 231, 288–299, https://doi.org/10.1016/j.chemgeo.2006.02.003.
- (2007) Simultaneous incorporation of Mn and Al in the goethite structure. Geochimica et Cosmochimica Acta, 71, 1009–1020, https://doi.org/10.1016/j. gca.2006.11.012.
- Alvarez, M., Sileo, E.E., and Rueda, E.H. (2008) Structure and reactivity of synthetic Co-substituted goethites. American Mineralogist, 93, 584–590, https:// doi.org/10.2138/am.2008.2608.
- Alvarez, M., Tufo, A.E., Zenobi, C., Ramos, C.P., and Sileo, E.E. (2015) Chemical, structural and hyperfine characterization of goethites with simultaneous incorporation of manganese, cobalt and aluminum ions. Chemical Geology, 414, 16–27, https://doi.org/10.1016/j.chemgeo.2015.08.022.
- Ammann, M.W., Brodholt, J.P., Wookey, J., and Dobson, D.P. (2010) First-principles constraints on diffusion in lower-mantle minerals and a weak D" layer. Nature, 465, 462–465, https://doi.org/10.1038/nature09052.
- Asta, M.P., Cama, J., Martínez, M., and Giménez, J. (2009) Arsenic removal by goothite and jarosite in acidic conditions and its environmental implications. Journal of Hazardous Materials, 171, 965–972, https://doi.org/10.1016/j. jhazmat.2009.06.097.
- Becker, U., Fernandez-Gonzalez, A., Prieto, M., Harrison, R., and Putnis, A. (2000) Direct calculation of thermodynamic properties of the barite/celestite solid solution from molecular principles. Physics and Chemistry of Minerals, 27, 291–300, https://doi.org/10.1007/s002690050258.
- Benny, S., Grau-Crespo, R., and de Leeuw, N.H. (2009) A theoretical investigation of α-Fe₂O₃-Cr₂O₃ solid solutions. Physical Chemistry Chemical Physics, 11, 808–815, https://doi.org/10.1039/B815907F.
- Blöchl, P.E. (1994) Projector augmented-wave method. Physical Review B: Condensed Matter, 50, 17953–17979, https://doi.org/10.1103/PhysRevB.50.17953.
- Burns, R.G. (1993) Mineralogical Applications of Crystal Field Theory, 576 p. Cambridge University Press.
- Carvalho-E-Silva, M.L., Ramos, A.Y., Tolentino, H.C.N., Enzweiler, J., Netto, S.M., and Do Carmo Martins Alves, M. (2003) Incorporation of Ni into natural goethite: An investigation by X-ray absorption spectroscopy. American Mineralogist, 88, 876–882, https://doi.org/10.2138/am-2003-5-617.
- Chatterjee, S. and Saha-Dasgupta, T. (2010) First-principles simulations of structural, electronic, and magnetic properties of vacancy-bearing Fe silicates. Physical Review B: Condensed Matter and Materials Physics, 81, 155105, https://doi.org/10.1103/PhysRevB.81.155105.
- Chernyshova, I.V., Ponnurangam, S., and Somasundaran, P. (2010) On the origin of an unusual dependence of (bio)chemical reactivity of ferric hydroxides on nanoparticle size. Physical Chemistry Chemical Physics, 12, 14045–14056, https://doi.org/10.1039/c0cp00168f.
- Christensen, A.N., Jensen, T.R., Bahl, C.R.H., and DiMasi, E. (2007) Nano size crystals of goethite, α-FeOOH: Synthesis and thermal transformation. Journal of Solid State Chemistry, 180, 1431–1435, https://doi.org/10.1016/j. jssc.2007.01.032.
- Ciobanu, C.L., Cook, N.J., Utsunomiya, S., Pring, A., and Green, L. (2011) Focused ion beam-transmission electron microscopy applications in ore mineralogy: Bridging micro- and nanoscale observations. Ore Geology Reviews, 42, 6–31, https://doi.org/10.1016/j.oregeorev.2011.06.012.
- Cornell, R.M. and Giovanoli, R. (1987) Effect of manganese on the transformation of ferrihydrite into goethite and jacobsite in alkaline media. Clays and Clay Minerals, 35, 11–20, https://doi.org/10.1346/CCMN.1987.0350102.
- Du, W., Xu, Y., and Wang, Y. (2008) Photoinduced degradation of orange II on

different iron (hydr)oxides in aqueous suspension: Rate enhancement on addition of hydrogen peroxide, silver nitrate, and sodium fluoride. Langmuir, 24, 175–181, https://doi.org/10.1021/la7021165.

- Gasser, U.G., Nuesch, R., Singer, M.J., and Jeanroy, E. (1999) Distribution of manganese in synthetic goethite. Clay Minerals, 34, 291–299, https://doi.org/ 10.1180/000985599546244.
- Georgiou, C.D., Sun, H.J., McKay, C.P., Grintzalis, K., Papapostolou, I., Zisimopoulos, D., Panagiotidis, K., Zhang, G., Koutsopoulou, E., Christidis, G.E., and others. (2015) Evidence for photochemical production of reactive oxygen species in desert soils. Nature Communications, 6, 7100, https://doi.org/ 10.1038/ncomms8100.
- Gialanella, S., Girardi, F., Ischia, G., Lonardelli, I., Mattarelli, M., and Montagna, M. (2010) On the goethite to hematite phase transformation. Journal of Thermal Analysis and Calorimetry, 102, 867–873, https://doi.org/10.1007/ s10973-010-0756-2.
- Giménez, J., Martínez, M., de Pablo, J., Rovira, M., and Duro, L. (2007) Arsenic sorption onto natural hematite, magnetite, and goethite. Journal of Hazardous Materials, 141, 575–580, https://doi.org/10.1016/j.jhazmat.2006.07.020.
- Granados-Correa, F., Corral-Capulin, N.G., Olguin, M.T., and Acosta-Leon, C.E. (2011) Comparison of the Cd(II) adsorption processes between boehmite (γ-AlOOH) and goethite (α-FeOOH). Chemical Engineering Journal, 171, 1027–1034, https://doi.org/10.1016/j.cej.2011.04.055.
- Huang, F., Chen, L., Wu, Z., and Wang, W. (2013) First-principles calculations of equilibrium Mg isotope fractionations between garnet, clinopyroxene, orthopyroxene, and olivine: Implications for Mg isotope thermometry. Earth and Planetary Science Letters, 367, 61–70, https://doi.org/10.1016/j.epsl.2013.02.025.
- Jain, A., Hautier, G., Ong, S.P., Moore, C.J., Fischer, C.C., Persson, K.A., and Ceder, G. (2011) Formation enthalpies by mixing GGA and GGA+U calculations. Physical Review B: Condensed Matter and Materials Physics, 84, 045115, https://doi.org/10.1103/PhysRevB.84.045115.
- Jung, D.Y. and Schmidt, M.W. (2011) Solid solution behaviour of CaSiO₃ and MgSiO₃ perovskites. Physics and Chemistry of Minerals, 38, 311–319, https:// doi.org/10.1007/s00269-010-0405-0.
- Jung, D.Y., Vinograd, V.L., Fabrichnaya, O.B., Oganov, A.R., Schmidt, M.W., and Winkler, B. (2010) Thermodynamics of mixing in MgSiO₃-Al₂O₃ perovskite and ilmenite from *ab initio* calculations. Earth and Planetary Science Letters, 295, 477–486, https://doi.org/10.1016/j.epsl.2010.04.026.
- Kakuta, S., Numata, T., and Okayama, T. (2014) Shape effects of goethite particles on their photocatalytic activity in the decomposition of acetaldehyde. Catalysis Science & Technology, 4, 164–169, https://doi.org/10.1039/C3CY00768E.
- Kaur, N., Grafe, M., Singh, B., and Kennedy, B. (2009) Simulations Incorporation of Cr, Zn, Cd, and Pb in the goethite structure. Clays and Clay Minerals, 57, 234–250, https://doi.org/10.1346/CCMN.2009.0570210.
- Klingelhöfer, G., DeGrave, E., Morris, R.V., Van Alboom, A., De Resende, V., De Souza, P., Rodionov, D., Schröder, C., Ming, D., and Yen, A. (2005) Mössbauer spectroscopy on Mars: Goethite in the Columbia Hills at Gusev crater. Hyperfine Interactions, 166, 549–554, https://doi.org/10.1007/s10751-006-9329-y.
- Kresse, G. and Furthmüller, J. (1996) Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. Physical Review B: Condensed Matter, 54, 11169–11186, https://doi.org/10.1103/PhysRevB.54.11169.
- Kresse, G. and Joubert, D. (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. Physical Review B: Condensed Matter, 59, 1758–1775, https://doi.org/10.1103/PhysRevB.59.1758.
- Kusuyama, T., Tanimura, K., and Sato, K. (2002) Adsorptive properties of Mn-substituted goethite particles for aqueous solutions of lead, copper, and zinc. Materials Transactions, 43, 455–458, https://doi.org/10.2320/matertrans.43.455.
- Lee, T.H., Lee, S.A., Park, H., Choi, M.J., Lee, D., and Jang, H.W. (2020) Understanding the enhancement of the catalytic properties of goethite by transition metal doping: Critical role of O* formation energy relative to OH* and OOH*. ACS Applied Energy Materials, 3, 1634–1643, https://doi.org/ 10.1021/acsaem.9b02140.
- Li, Y., Xu, X., Li, Y., Ding, C., Wu, J., Lu, A., Ding, H., Qin, S., and Wang, C. (2018) Absolute band structure determination on naturally occurring rutile with complex chemistry: Implications for mineral photocatalysis on both Earth and Mars. Applied Surface Science, 439, 660–671, https://doi.org/10.1016/j. apsusc.2017.12.195.
- Liu, G., Zhu, D., Zhou, W., Liao, S., Cui, J., Wu, K., and Hamilton, D. (2010) Solid-phase photocatalytic degradation of polystyrene plastic with goethite modified by boron under UV–vis light irradiation. Applied Surface Science, 256, 2546–2551, https://doi.org/10.1016/j.apsusc.2009.10.102.
- Liu, G., Liao, S., Zhu, D., Liu, L., Cheng, D., and Zhou, H. (2011) Photodegradation of aniline by goethite doped with boron under ultraviolet and visible light irradiation. Materials Research Bulletin, 46, 1290–1295, https://doi.org/ 10.1016/j.materresbull.2011.03.033.
- Liu, X., Lu, X., Liu, X., and Zhou, H. (2015) Atomistic simulation on mixing thermodynamics of calcite-smithsonite solid solutions. American Mineralogist, 100, 172–180, https://doi.org/10.2138/am-2015-4815.
- Liu, X., Vinograd, V.L., Lu, X., Leonenko, E.V., Eremin, N.N., Wang, R., and Winkler, B. (2016) Thermodynamics of mixing in an isostructural solid solu-

tion: Simulation methodologies and application to the rutile-cassiterite system. American Mineralogist, 101, 1197–1206, https://doi.org/10.2138/am-2016-5490.

- Liu, H., Lu, X., Li, M., Zhang, L., Pan, C., Zhang, R., Li, J., and Xiang, W. (2018) Structural incorporation of manganese into goethite and its enhancement of Pb(II) adsorption. Environmental Science & Technology, 52, 4719–4727, https://doi.org/10.1021/acs.est.7b05612.
- Majzlan, J., Grevel, K.D., and Navrotsky, A. (2003) Thermodynamics of Fe oxides: Part II. Enthalpies of formation and relative stability of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and maghemite (γ-Fe₂O₃). American Mineralogist, 88, 855–859, https://doi.org/10.2138/am-2003-5-614.
- Mameri, Y., Debbache, N., Benacherine, M., Seraghni, N., and Schili, T. (2016) Heterogeneous photodegradation of paracetamol using goethite/H₂O₂ and goethite/oxalic acid systems under artificial and natural light. Journal of Photochemistry and Photobiology A Chemistry, 315, 129–137, https://doi.org/ 10.1016/j.jphotochem.2015.09.019.
- Mamindy-Pajany, Y., Hurel, C., Marmier, N., and Romeo, M. (2011) Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility. Desalination, 281, 93–99, https://doi.org/10.1016/j.desal.2011.07.046.
- Manceau, A., Schlegel, M.L., Musso, M., Sole, V.A., Gauthier, C., Petit, P.E., and Trolard, F. (2000) Crystal chemistry of trace elements in natural and synthetic goethite. Geochimica et Cosmochimica Acta, 64, 3643–3661, https://doi.org/ 10.1016/S0016-7037(00)00427-0.
- Murakami, N., Matsuo, T., Tsubota, T., and Ohno, T. (2011) Photocatalytic reaction over iron hydroxides: A novel visible-light-responsive photocatalyst. Catalysis Communications, 12, 341–344, https://doi.org/10.1016/j.catcom.2010.10.012.
- Nagai, T., Kagi, H., and Yamanaka, T. (2003) Variation of hydrogen bonded O···O distances in goethite at high pressure. American Mineralogist, 88, 1423–1427, https://doi.org/10.2138/am-2003-1005.
- Nguyen, N.H.A., Von Moos, N.R., Slaveykova, V.I., Mackenzie, K., Meckenstock, R.U., Thümmler, S., Bosch, J., and Ševců, A. (2018) Biological effects of four iron-containing nanoremediation materials on the green alga *Chlamydomonas* sp. Ecotoxicology and Environmental Safety, 154, 36–44, https://doi.org/ 10.1016/j.ecoenv.2018.02.027.
- Oganov, A.R., Martonák, R., Laio, A., Raiteri, P., and Parrinello, M. (2005) Anisotropy of Earth's D" layer and stacking faults in the MgSiO₃ post-perovskite phase. Nature, 438, 1142–1144, https://doi.org/10.1038/nature04439.
- Otte, K., Schmahl, W.W., and Pentcheva, R. (2012) Density functional theory study of water adsorption on FeOOH surfaces. Surface Science, 606, 1623–1632, https://doi.org/10.1016/j.susc.2012.07.009.
- Perdew, J.P., Burke, K., and Ernzerhof, M. (1996) Generalized gradient approximation made simple. Physical Review Letters, 77, 3865–3868, https:// doi.org/10.1103/PhysRevLett.77.3865.
- Popescu, V. and Zunger, A. (2012) Extracting *E* versus *k* effective band structure from supercell calculations on alloys and impurities. Physical Review B: Condensed Matter and Materials Physics, 85, 085201, https://doi.org/10.1103/ PhysRevB.85.085201.
- Rahimi, S., Moattari, R.M., Rajabi, L., Derakhshan, A.A., and Keyhani, M. (2015) Iron oxide/hydroxide (a, γ-FeOOH) nanoparticles as high potential adsorbents for lead removal from polluted aquatic media. Journal of Industrial and Engineering Chemistry, 23, 33–43, https://doi.org/10.1016/j.jiec.2014.07.039.
- Ravina, M., Campanella, L., and Kiwi, J. (2002) Accelerated mineralization of the drug Diclofenac via Fenton reactions in a concentric photo-reactor. Water Research, 36, 3553–3560, https://doi.org/10.1016/S0043-1354(02)00075-1.
- Rout, K., Dash, A., Mohapatra, M., and Anand, S. (2014) Manganese doped goethite: Structural, optical and adsorption properties. Journal of Environmental Chemical Engineering, 2, 434–443, https://doi.org/10.1016/j.jece.2014.01.001.
- Ruiz-Hernandez, S.E., Grau-Crespo, R., Ruiz-Salvador, A.R., and De Leeuw, N.H. (2010) Thermochemistry of strontium incorporation in aragonite from atomistic simulations. Geochimica et Cosmochimica Acta, 74, 1320–1328, https://doi.org/ 10.1016/j.gca.2009.10.049.
- Scheinost, A.C., Stanjek, H., Schulze, D.G., Gasser, U., and Sparks, D.L. (2001) Structural environment and oxidation state of Mn in goethite-groutite solidsolutions. American Mineralogist, 86, 139–146, https://doi.org/10.2138/am-2001-0115.
- Schuttlefield, J.D., Sambur, J.B., Gelwicks, M., Eggleston, C.M., and Parkinson, B.A. (2011) Photooxidation of chloride by oxide minerals: Implications for perchlorate on Mars. Journal of the American Chemical Society, 133, 17521–17523, https://doi.org/10.1021/ja2064878.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767, https://doi.org/10.1107/S0567739476001551.

- Sherman, D.M. (2005) Electronic structures of iron(III) and manganese(IV) (hydr)oxide minerals: Thermodynamics of photochemical reductive dissolution in aquatic environments. Geochimica et Cosmochimica Acta, 69, 3249–3255, https://doi.org/10.1016/j.gca.2005.01.023.
- Shkrob, I.A., Marin, T.M., Adhikary, A., and Sevilla, M.D. (2011) Photooxidation of nucleic acids on metal oxides: Physico-chemical and astrobiological perspectives. The Journal of Physical Chemistry C, 115, 3393–3403, https:// doi.org/10.1021/jp110682c.
- Sileo, E.E., Alvarez, M., and Rueda, E.H. (2001) Structural studies on the manganese for iron substitution in the synthetic goethite-jacobsite system. International Journal of Inorganic Materials, 3, 271–279, https://doi.org/10.1016/ S1466-6049(01)00035-6.
- Singh, B., Sherman, D.M., Gilkes, R.J., Wells, M.A., and Mosselmans, J.F.W. (2002) Incorporation of Cr, Mn and Ni into goethite (α-FeOOH): Mechanism from extended X-ray absorption fine structure spectroscopy. Clay Minerals, 37, 639–649, https://doi.org/10.1180/000985502374066.
- Stiers, W. and Schwertmann, U. (1985) Evidence for manganese substitution in synthetic goethite. Geochimica et Cosmochimica Acta, 49, 1909–1911, https:// doi.org/10.1016/0016-7037(85)90085-7.
- Vinograd, V. and Winkler, B. (2010) An efficient cluster expansion method for binary solid solutions: Application to the halite-silvite, NaCl-KCl, system. Reviews in Mineralogy and Geochemistry, 71, 413–436, https://doi.org/10.2138/ rmg.2010.71.19.
- Vinograd, V., Burton, B., Gale, J., Allan, N., and Winkler, B. (2007) Activity– composition relations in the system CaCO₃-MgCO₃ predicted from static structure energy calculations and Monte Carlo simulations. Geochimica et Cosmochimica Acta, 71, 974–983, https://doi.org/10.1016/j.gca.2006.11.008.
- Vinograd, V., Sluiter, M., and Winkler, B. (2009) Subsolidus phase relations in the CaCO₃-MgCO₃ system predicted from the excess enthalpies of supercell structures with single and double defects. Physical Review B: Condensed Matter and Materials Physics, 79, 104201, https://doi.org/10.1103/PhysRevB.79.104201.
- Wang, Q., Grau-Crespo, R., and de Leeuw, N.H. (2011) Mixing thermodynamics of the calcite-structured (Mn,Ca)CO₃ solid solution: A computer simulation study. The Journal of Physical Chemistry B, 115, 13854–13861, https://doi.org/ 10.1021/jp200378q.
- West, A.R. (1984) Solid State Chemistry and Its Applications, 592 p. Wiley.
- Wu, W.C., Wang, S.L., Tzou, Y.M., Chen, J.H., and Wang, M.K. (2007) The adsorption and catalytic transformations of chromium on Mn substituted goethite. Applied Catalysis B: Environmental, 75, 272–280, https://doi.org/10.1016/j. apcatb.2007.04.026.
- Wu, Y.F., Fougerouse, D., Evans, K., Reddy, S.M., Saxey, D.W., Guagliardo, P., and Li, J.W. (2019) Gold, arsenic, and copper zoning in pyrite: A record of fluid chemistry and growth kinetics. Geology, 47, 641–644, https://doi.org/ 10.1130/G46114.1.
- Zhang, H., Bayne, M., Fernando, S., Legg, B., Zhu, M., Penn, R.L., and Banfield, J.F. (2011) Size-dependent bandgap of nanogoethite. The Journal of Physical Chemistry C, 115, 17704–17710, https://doi.org/10.1021/jp205192a.
- Zhao, H., Yang, Y., Shu, X., Wang, Y., and Ran, Q. (2018) Adsorption of organic molecules on mineral surfaces studied by first-principle calculations: A review. Advances in Colloid and Interface Science, 256, 230–241, https://doi.org/ 10.1016/j.cis.2018.04.003.
- Zhou, X., Yang, H., Wang, C., Mao, X., Wang, Y., Yang, Y., and Liu, G. (2010) Visible light induced photocatalytic degradation of rhodamine B on onedimensional iron oxide particles. The Journal of Physical Chemistry C, 114, 17051–17061, https://doi.org/10.1021/jp103816e.

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Endnote:

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