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Quantum mechanical method for estimating ionicity of spinel ferrites

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ABSTRACT

The ionicity (0.879) of cubic spinel ferrite Fe_3O_4 has been determined, using both experimental magnetization and density of state calculations from the density functional theory. Furthermore, a quantum mechanical estimation method for the ionicity of spinel ferrites is proposed by comparing the results from Phillips' ionicity. On the basis of this, ionicities of the spinel ferrites MFe_2O_4 ($M=$Mn, Fe, Co, Ni, Cu) are calculated. As an application, the ion distribution at (A) and [B] sites of $(A)[B]_2O_4$ spinel ferrites MFe_2O_4 ($M=$Fe, Co, Ni, Cu) are calculated using current ionicity values.

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1. Introduction

It is well known that there are both ionic and covalent bonds in oxides and that ionicity has been defined as a fraction of ionic bonds. Phillips introduced a review of studies on the ionicity of simple compounds until 1970 [1]. In recent decades, ionicity has been studied further [2–5]. Abu-Farsahk and Qteish [2] calculated the ionicities of some simple compounds on the centers of maximally localized Wannier functions. Thomas and Pollini [3] investigated ionicities of some transimetal halides. Petit et al. [4] calculated the electronic structure and ionicity of simple actinide oxides from first principle. Chelikowsky and Burdett [5] calculated ionicity of some simple oxides and sulfides.

The structure, magnetic properties [6,7], dielectric properties [8,9] and magneto–optical properties [10,11] of spinel ferrites have been investigated widely. Ferrites in the form of $(A)[B]_2O_4$ with spinel structure are based on a face-centered cubic lattice of the oxygen ions in which the metal ions are located at intervals of oxygen ions. Site (A) is a tetrahedral site with 4 neighboring oxygen ions and site [B] is an octahedral site with 6 neighboring oxygen ions. Oudet [12] discussed valency and ionicity in RCr_2O_4 and RV_2O_4 type spinels. He supposed that all tetrahedral sites were occupied by one kind of cation with R^{2+} (normal spinel structure), Cr^{3+} or V^{3+} (inverse spinel structure).

However, many recent studies have neglected to consider ionicity in their discussion about compounds. That is to say, they have considered only that there are ionic bonds and no covalent bonds, due to that there has been no convenient method for estimating the ionicity for multi-atom compounds.

In earlier works [13–16], we proposed a quantum-mechanical method for estimating the cation distribution in cubic spinel ferrites, where materials were treated as ionic compounds without covalent bonds. In this paper, using both magnetization and density of states calculated by the density functional theory, ionicity of cubic spinel ferrite Fe_3O_4 is determined. Furthermore, a quantum mechanical method for ionicity of spinel ferrites was proposed by comparing the Phillips' ionicity data [1]. On the basis of this, we improved the quantum-mechanical method for estimating the cation distribution in cubic spinel ferrites [13–16], and re-calculated the cation distribution of the spinel ferrites MFe_2O_4 ($M=$Fe, Co, Ni, Cu). We believe that our treatment method about cation distribution of spinel ferrites with ionicity will also be beneficial for magneto–optical and dielectric investigations of spinel ferrite. This work may become a clue for investigations of compounds with other structures.

2. Calculation and discussion about densities of states (DOS) for valency electrons in cubic spinel ferrite Fe_3O_4

For this study, we calculated the density of states (DOS) for valency electrons in cubic spinel ferrite Fe_3O_4 using the plane–wave pseudopotential density functional theory (DFT) method as implemented in the Cambridge Serial Total Energy Package (CASTEP) [17,18] program. The electronic structure was calculated using local density approximations with the Perdew and Wang (1991) version of the generalized gradient approximation (PW91-GGA) [19] combined with on-site Coulomb interaction U (LDA+U) [20,21]. The parameter U was employed to explore effects of a Coulomb correction to the localized 3d electrons [22]. The effective correlation of U that was used was 5.0 and 4.0 eV for site (A) and site [B] ions, respectively. These values are close to

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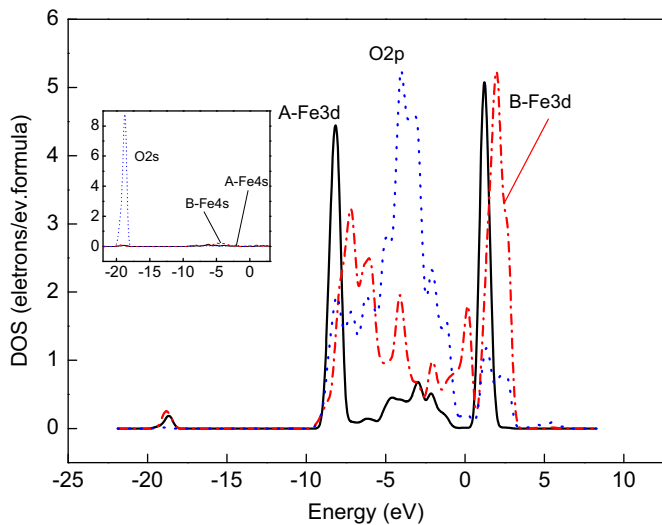 *E-mail address:* tanggd@mail.hebtu.edu.cn (G.D. Tang).

Fig.1. Density of states of valency electrons of Fe and O ions in cubic spinel ferrite Fe_3O_4.

those found by Antonov et al. [23] for doped bulk Fe_3O_4 and Zhu et al. [24] for surface Fe_3O_4. Ultrasoft pseudopotentials with a cutoff energy of 500 eV were used to describe the electron–ion interaction and pseudoatomic calculations were performed for the O $2s^24p^4$, Fe $3d^64s^2$ configurations. Parameters for the convergence tolerance were 5.0×10^{-7} eV/atom for the total energy and 8.14×10^{-9} eV for the Fermi energy. A Gaussian smearing scheme was used with 0.1 eV for the smearing width. A $6 \times 6 \times 6$ Monkhorst–Pack scheme was used to produce a uniform grid of k-points along the three axes in reciprocal space. Magnetic moments of the metal cations were evaluated using spin-polarized DFT calculations. The initial spins were those recommended by the CASTEP package for use in spin-polarized calculations.

For cubic spinel Fe_3O_4, the DOSs of Fe 3d and O 2p in Fe_3O_4 are shown in Fig. 1, in which the inset shows the DOSs of Fe 4s and O 2s. It can be calculated, below the Fermi energy level (the zero point of energy), that the number ratio of Fe 4s to Fe 3d electrons is about 5%, so that Fe 4s electrons can be neglected. About 96% of O 2s electrons distribute below -17 eV, which does not permit orbit hybridization with the metal cations. Near the Fermi energy level, there are only the DOSs of the Fe 3d and O 2p orbitals. Therefore, orbit hybridization between Fe cations and oxygen anions will occur between Fe 3d and O 2p. Therefore, the magnetic order of the material is affected since the itinerant electrons in the material hop between the Fe 3d and O 2p levels.

The average number, n, of 3d electrons in Fe_A [at the (A) sites] and Fe_B ions {at the [B] sites} in Fe_3O_4 are 5.975 and 6.089, respectively that are calculated to lie below the Fermi energy levels in Fig. 1, and the average number of 2p electrons of O ions is 4.894. It can be seen that the average number of O 2p electrons is lower than 6 in O^{2-} anion in the traditional view, while the average number of 3d electrons in Fe is $6.051[=(5.975+6.089 \times 2)/3$, one Fe_A and two Fe_B], being more than $5.33[=(6+5 \times 2)/3$, one Fe^{2+} and two Fe^{3+}] as in the traditional view when the valence of the oxygen anion is -2. That is to say, the valences of cations and anions as determined by the DOS patterns are obviously smaller than in the traditional view. The reason for this is that the second electronic affinity energy of oxygen (8.08 eV) is far smaller than the third ionization energy of Fe (30.65 eV), with the result that the Fe^{3+} ions are not easy to form. The content of ionic bonds in Fe_3O_4 is thus obviously less than 100%.

According to the traditional view, in Fe_3O_4 with an $(A)[B]_2O_4$ inverse spinel structure, all cation magnetic moments are parallel at low temperature in the (A) sites and [B] sites taken separately,

while magnetic moments of ions in the (A) sites are antiparallel to those in the [B] sites. Using the above calculated 3d electron numbers for Fe, it can be calculated that the moment per formula of Fe_3O_4 is 3.8 μ_B, which is obviously smaller than experimental value of 4.2 μ_B [6,7]. Therefore, the above calculated numbers of Fe 3d need a correction to more closely match the experimentally measured magnetic moment.

In order to provide a more accurate analysis, we will define the magnetic moment of one iron cation at the (A) site to be m_A (μ_B), which is antiparallel to that at [B] sites, m_B (μ_B). If the experimental moment per formula, 4.2 μ_B, is to be satisfied, then

$$2m_B - m_A = 4.2 \tag{1}$$

And the average content ratio (n_A/n_B) of 3d electrons in the iron cations at (A) and [B] sites is set to be equal to the calculated value,

$$\frac{n_A}{n_B} = \frac{5.975}{6.089} \tag{2}$$

According to Hund′ rules and the traditional ferrite theory [6,7],

$$m_A = 10 - n_A, \quad m_B = 10 - n_B, \tag{3}$$

and we obtain,

$$n_A = 5.584, \quad n_B = 5.692; \quad m_A = 4.416, \quad m_B = 4.308, \tag{4}$$

which indicates that the 3d electron numbers at the (A) sites and the [B] sites, 5.584 and 5.692, are obviously lower than calculated values, 5.975 and 6.089, and are obviously higher than that in traditional view of 5 (there is one Fe^{3+} at (A) site, per formula) and 5.5 (there are one Fe^{3+} and one Fe^{2+} at [B] sites). The reason is that the ionicity of an oxide cannot reach 100%.

If other 3d electrons and all the 4s electrons of the iron cations are obtained by oxygen anions, then the average valences of the iron cations at the (A) and [B] sites are $+2.416(=8-n_A$, the total number of 3d and 4s electrons in one Fe atom is 8) and $+2.308(=8-n_B)$, respectively. These valences are very close to the results calculated by Jeng et al. [25]. It is thus easy to calculate that the content ratio of Fe_A^{3+} to Fe_A^{2+} cations is 0.416/0.584, and the content ratio of Fe_B^{3+} to Fe_B^{2+} cations is 0.308/0.692. That is to say, the number of Fe^{3+} cations for every Fe_3O_4 formula is only $1.032(=0.416+0.308 \times 2)$, rather than 2 in traditional view. It is also easy to calculate that the average valence of oxygen anions is $-1.758[=(2.416+2 \times 2.308)/4]$, and therefore the ionicity of Fe_3O_4 is 0.879 [$=1.758/2$].

3. A quantum mechanical estimation method for ionicity of spinel ferrites

In the quantum mechanical model to estimate the cation distribution [13–16], we assume that there is a square potential barrier between a cation–anion pair. The height of the potential barrier is proportional to the ionization energy of the last ionized electron, and the width of the potential barrier is related to the distance between neighboring cations and anions. The content ratio (R) of the different cations, which is therefore related to the probability of their last ionized electrons penetrating the potential barrier, can be derived, and takes the form

$$R = \frac{T_C}{T_D} = \frac{V_D}{V_C} \exp\left[10.24(r_D V_D^{1/2} - c r_C V_C^{1/2})\right], \tag{5}$$

where nanometers (nm) and electron–volts (eV) are used as the units of length and energy, respectively.

According to the results from Phillips [1], strontic compounds have the maximum ionicity in II–VI compounds, as shown in Table 1. Next, by fitting the ionicities of strontium compounds, we show that Eq. (5) can be used to estimate ionicity.