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Jinbo Yang

M. S. Kim

Qingsheng Cai

X.-D. Zhou
Missouri University of Science and Technology

et. al. For a complete list of authors, see *https://scholarsmine.mst.edu/matsci_eng_facwork/1453*

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Study of the electronic structure of CaFeO$_3$

J. B. Yang and M. S. Kim
Materials Research Center, University of Missouri-Rolla, Rolla, Missouri 65409 and Department of Physics, University of Missouri-Rolla, Rolla, Missouri 65409

Q. Cai
Department of Physics, University of Missouri-Columbia, Columbia, Missouri 65211

X. D. Zhou and H. U. Anderson
Materials Research Center, University of Missouri-Rolla, Rolla, Missouri 65409

W. J. James and W. B. Yelon
Materials Research Center, University of Missouri-Rolla, Rolla, Missouri 65409 and Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65409

We have studied the charge disproportionation phenomenon in CaFeO$_3$ using the local-spin density approximation with the on-site Coulomb interaction parameter U and exchange parameter J. The calculation reveals that the total number of the $3d$ electrons is about 5.1 for both Fe(1)(Fe^{5+}) and Fe(2)(Fe^{3+}) atoms, and that there are about 0.25 electron holes in the O-$2p$ band. Therefore, the charge disproportionation can be more accurately described as $2d^5L(\mathrm{Fe}^{4+})=d^5L^2(\mathrm{Fe}^{5+})+d^5(\mathrm{Fe}^{3+})$, where L denotes a hole in the oxygen $2p$ band, instead of $2d^4(\mathrm{Fe}^{4+})=d^3(\mathrm{Fe}^{5+})+d^5(\mathrm{Fe}^{3+})$. The hybridization between the Fe-$3d$ and O-$2p$ orbitals is stronger for Fe(1) than for Fe(2) due to the shorter Fe(1)–O bond. The hyperfine magnetic field contributed from conduction electron polarization is larger for Fe(2), resulting from a stronger s-d hybridization between the s orbital of Fe(2) and the d orbitals of its neighboring Fe(1) atoms. The on-site Coulomb repulsion and the exchange interaction increase the splitting between the occupied spin up and unoccupied spin down bands of Fe atoms. Fe-$3d$ electrons become localized and the occupied d-band shifts to a lower energy range, even below the O-$2p$ level. The calculated magnetic moments, hyperfine fields, and electron charge density agree well with the experimental data. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1854275]

Charge ordering (CO) and charge disproportionation (CD) in the perovskite oxides, e.g., CaFeO$_3$, have been extensively studied.[1–5] CaFeO$_3$ shows CD below 290 K with a change of crystal structure from orthorhombic, space group *Pbnm*, at room temperature, to monoclinic, space group $P2_1/n$ with two different Fe sites Fe(1) and Fe(2), at low temperature.[2,5] However, the mechanism of CD is still controversial.[6] Mössbauer data at 4.2 K have revealed a CD which was thought to be $2d^4(\mathrm{Fe}^{4+})=d^3(\mathrm{Fe}^{5+})+d^5(\mathrm{Fe}^{3+})$.[1] However, study of the hyperfine field as a function of temperature has shown that this charge disproportionation occurs in varying degrees, corresponding to the charge states of Fe$^{4-\delta}$ and Fe$^{4+\delta}$.[7] Recently, Matsuno *et al.*[4] suggested that the charge disproportionation can be correctly described as $2d^5\underline{L} \rightarrow d^5\underline{L}^2+d^5$ rather than $2d^4 \rightarrow d^3+d^5$, where $\underline{L}$ denotes a hole in the oxygen $2p$ band. In this paper, we calculated the electronic structures using the local-spin density approximation (LSDA) with the on-site Coulomb interaction parameter U and exchange parameter J. Based on the calculated electronic structures, we present the theoretical results for the magnetic moments, hyperfine magnetic field, and the electron charge density for CaFeO$_3$.

The self-consistent band structure has been calculated using the WIEN2K code.[8] The full-potential linearized augmented-plane-wave method is employed using the LSDA, as well as the LSDA+U scheme. At 300 K, CaFeO$_3$ has the GdFeO$_3$ structure, space group *Pbnm* with lattice parameters $a=5.326$ Å, $b=7.539$ Å, and $c=7.539$ Å. At 15 K, the crystal structure changes to space group $P2_1/n$ with $a=5.311$ Å, $b=5.347$ Å, and $c=7.520$ Å, and $\beta=90.065°$.[5] The electronic structures were calculated for the antiferromagnetic CaFeO$_3$ with reported lattice parameters at RT and low temperature in order to understand the mechanism of CO and CD.

The first step in our study was to perform the LSDA calculation ($U, J=0.0$ eV) for the low temperature structure of CaFeO$_3$. The calculated density of states (DOS) of CaFeO$_3$ without the onsite Coulomb parameter U resulted in a metallic band being obtained for the ground state. There is no energy gap in the electronic structures. The d states of Fe(1) and Fe(2) dominate the DOS of Fe atoms. A strong hybridization appears between the Fe-$3d$ and O-$2p$ orbitals. The calculated magnetic moments and hyperfine fields of the Fe atoms in CaFeO$_3$ low temperature structure are listed in Table I. The local magnetic moments and hyperfine fields of the Fe atoms were underestimated when compared to the experimental values.[1,5] It is found that the LSDA does not explain well the physical properties of CaFeO$_3$. In order to explain the discrepancy between experimental and theoretical results, the orbital and dipole contributions to the magnetic moments and the hyperfine fields of Fe were also calculated. However, the orbital and dipole contributions are too

TABLE I. Calculated magnetic moments M (in μ_B), H_{FC} (in T), and its valence and core contributions for Fe(1) and Fe(2) atoms in CaFeO$_3$ low temperature structure with different on-site Coulomb parameters U. The intra-atomic exchange parameter J is fixed at 0.07 Ry. The experimental hyperfine fields H_{hf} (Expt.) are from Ref. 1. The experimental magnetic moments M (Expt.) are given for both spiral and sinusoidal models from Ref. 5.

U(Ry)	0.0	0.3	0.4	0.59
		Fe(1)		
M (μ_B)	2.096	2.206	2.409	2.991
M(Expt.) (μ_B)			2.38/2.70	
H_{FC} (T)	−23.3	−24.3	−25.1	−27.5
$H_{FC,core}$ (T)	−27.0	−25.5	−27.8	−34.8
$H_{FC,val}$ (T)	3.7	1.2	2.7	7.3
H_{hf}(Expt.) (T)			28.4	
		Fe(2)		
M (μ_B)	3.096	3.812	3.927	4.096
M(Expt.) (μ_B)			3.47/3.52	
H_{FC} (T)	−23.7	−29.9	−31.6	−35.5
$H_{FC,core}$ (T)	−40.3	−45.4	−46.8	−48.9
$H_{FC,val}$ (T)	16.6	15.5	15.2	13.4
H_{hf} (Expt.) (T)			41.9	

small to account for the differences. It is known that the $3d$ electron-electron exchange interactions are strong in the transition metal oxides, which is not considered properly in the LSDA.[9] Therefore, the differences between theoretical and experimental results may have arisen by not taking into account the Coulomb interaction. Accordingly, we calculated the electronic structures of CaFeO$_3$ using the LDA+U method. Figure 1 is the DOS of CaFeO$_3$ calculated with the on-site Coulomb parameter U=0.40 Ry (5.4 eV) and the intra-atomic exchange parameter J=0.07 Ry (0.95 eV), respectively. As shown in Fig. 1, the key features near the E_f are the O($2p$) and Fe($3d$) orbitals with an energy gap occurring in the middle of the Fe-$3d$ band. Compared to the LSDA calculation (U,J=0.0 eV), the Fe-$3d$ bands have shifted to the lower energy part with respect to the O-$2p$ states. Both the e_g and t_{2g} spin down bands of Fe were pushed up by the Coulomb interaction, and are nearly unoccupied. The dependence of the calculated local magnetic moments and hyperfine fields of the different Fe atoms on the Coulomb interaction parameter U are shown in Table I. Some available experimental hyperfine fields are included in Table I. The calculated magnetic moments and hyperfine fields agree well with the experimental data as U=0.59 Ry (8.0 eV).[1,5] We also found that the occupied Fe-$3d$ states are further separated from the unoccupied ones, and that the d state becomes more localized as U increases. Accordingly, the CO states are characterized by the strong hybridization between the Fe-$3d$ and O-$2p$ orbitals, which makes for a wide d-p band spreading from −7.5 to 0 eV. The hybridization between the Fe-$3d$ and O-$2p$ orbitals is larger for Fe(1) than that for Fe(2) due to the shorter bond length of Fe(1)–O. This difference in the hybridization between Fe and O leads to CD and CO in CaFeO$_3$ at low temperature. For comparison, we calculated the band structures for the crystal structure at room temperature. Fe atoms exhibit a single magnetic moment of
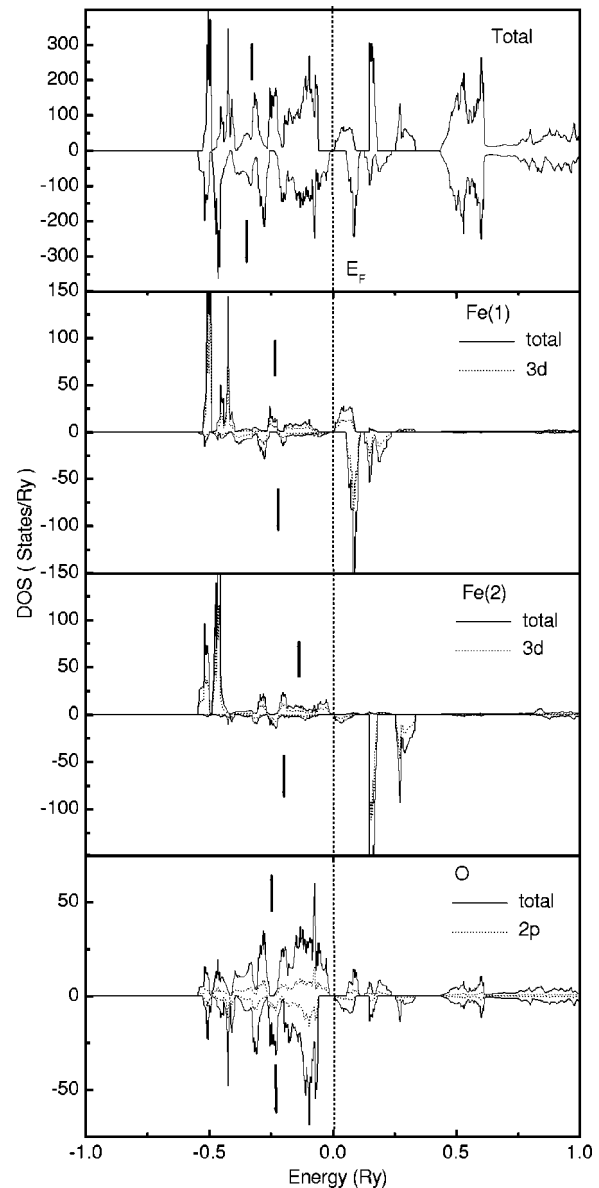

FIG. 1. The total and partial DOS of CaFeO$_3$ low temperature structure with U=0.40 Ry and J=0.07 Ry.

$3.7\mu_B$ in the orthorhombic CaFeO$_3$. This suggests that the change in the crystal structure affects the hybridization between Fe and O, and thus causes the CO to occur at low temperatures. The Fermi level lies in the band gap, which can explain the metal to insulator transition at low temperature in CaFeO$_3$.

In Table II, we list some electronic structure parameters

TABLE II. Number of Fe-$3d$ electrons and magnetic moments for two iron sites in CaFeO$_3$ low temperature structure.

	$n_d^\uparrow$	$n_d^\downarrow$	$n_d^\uparrow + n_d^\downarrow$	$n_d^\uparrow - n_d^\downarrow$
		U=0.0 Ry, J=0.0 Ry		
Fe(1)	3.609	1.525	5.134	2.094
Fe(2)	4.109	1.054	5.163	3.055
		U=0.4 Ry, J=0.07 Ry		
Fe(1)	3.720	1.317	5.037	2.403
Fe(2)	4.501	0.599	5.100	3.902

calculated for the low temperature structure. The average number of the Fe-3d electrons in the muffin-tin spheres is about 5.1 for both Fe(1) and Fe(2) atoms, corresponding to a valence state of Fe-3d^5. We note that the total number of $3d$ electrons shows a weak dependence on U. There are about 0.25 holes in the O-2p states, and total of 1.5 holes can be attained for each Fe atom with six neighboring O atoms. This suggests that the CO states are characterized by Fe-3d^5 and that the charge disproportionation can be more accurately described as $2d^5L(Fe^{4+})=d^5L^2(Fe^{5+})+d^5(Fe^{3+})$, rather than $2d^4(Fe^{4+})=d^3(Fe^{5+})+d^5(Fe^{3+})$.

Furthermore, more details of the electron interactions in CaFeO$_3$ can be provided from the calculated hyperfine field. We decompose H_{FC} into two parts, H_{FC}^{core} and H_{FC}^{val}. H_{FC}^{core} is the contribution from the s core electrons due to the polarized d electrons affecting the polarization of the core electrons. H_{FC}^{val} comes from the polarization of the valence electrons. The calculated H_{FC}^{core} and H_{FC}^{val} contributions to H_{FC} are listed in Table I. Generally, H_{FC}^{core} is proportional to the local magnetic moments of the Fe atoms. Using the calculated values in Table I, the proportionality coefficients are estimated to be about $-10T/\mu_B$ for both Fe(1) and Fe(2) atoms in CaFeO$_3$. This indicates both Fe(1) and Fe(2)-3d electrons have almost the same effects on the polarizations of the core s electrons of the Fe atoms. The calculated H_{FC}^{val} values of the Fe(2) atoms are higher than those of the Fe(1) and have opposite sign to H_{FC}^{core} due to the reversed polarization direction of the s-d hybridization between Fe(1) and Fe(2) atoms. These values differ from the normal value of the 3d metals (-5 T) because of the different magnetic exchange interactions in CaFeO$_3$.

H_{FC}^{val} consists of two terms, one is the local valence hyperfine field $H_{FC}^{l,val}$ which comes from the s-d exchange interaction within the atoms and is proportional to the local magnetic moments μ_s of the s electrons (normally μ_s is very small); another is the transferred hyperfine field $H_{FC}^{t,val}$ which comes from the s-d hybridization between the s orbitals of the atoms and the spin-polarized d orbitals of the neighboring atoms. Thus, H_{FC}^{val} may reveal s-d hybridization among the metal atoms. As for CaFeO$_3$, the s-d hybridization is effected through the Fe–O–Fe bond. The H_{FC}^{val} of Fe(2) atoms is much larger than that of Fe(1) atoms, suggesting a strong s-d hybridization occurring within the Fe(2)–Fe(1) atoms through oxygen. This effect causes Fe-3d electrons to be more localized and to have higher magnetic moments for Fe(2). Due to a shorter Fe(1)–O distance, the strong shielding effect of oxygen surrounding Fe(1) reduces the s-d interactions within Fe(1)–Fe(2) and results in a small positive H_{FC}^{val} at the Fe(1) sites, which differs greatly from that at Fe(2) sites. This is confirmed by the charge density plot in Fig. 2.
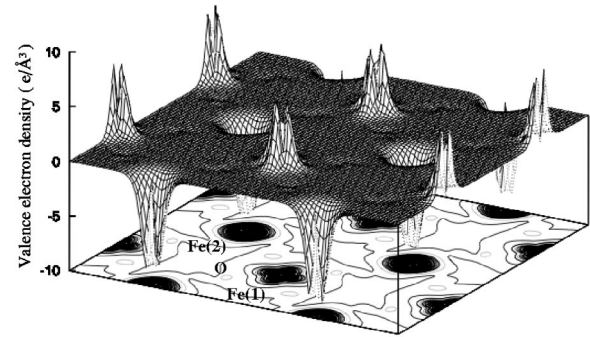

FIG. 2. The contours of net valence electron density (spin down–spin up) in the x-y plane for CaFeO$_3$ low temperature structure.

Figure 2 illustrates the magnetic behavior by plotting contours of the valence electron spin density in the x-y plane. The spin density of Fe(2) is larger and dominated by the occupied e_g orbitals (e.g., d_{xy}), whereas the spin density of Fe(1) is t_{2g}-like. An asymmetry in the oxygen density is visible in Fig. 2, and a small but nonvanishing polarization on the oxygen ion is also observed, which is nearer to Fe(1) due to the strong hybridization between Fe(1) and oxygen. This is consistent with the experimental pattern.[2]

Based on the calculated electronic structures of CaFeO$_3$, it is found that the charge disproportionation of CaFeO$_3$ can be described as $2d^5L(Fe^{4+})=d^5L^2(Fe^{5+})+d^5(Fe^{3+})$. The change of the crystal structure accompanies the charge deformation and leads to the charge disproportionation at low temperatures. The Fe-3d and O-2p interaction, as well as the s-d interaction between Fe(1) and Fe(2) through oxygen atoms, is the key to an understanding of CD and CO in CaFeO$_3$.

ACKNOWLEDGMENTS

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