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## ガラスの構造研究

### Study on the Structure of Glass

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#### Introduction

Recent progress in materials synthesis has led to a variety of nanostructures whose optical, electrical and magnetic properties are very different from those of bulk structures. This also reveals anomalous aspects of well understood phenomena of condensed matter physics. One of the interesting examples of the anomalies found in nanoscale oxides is the so-called d<sup>0</sup> ferromagnetism, which is referred to as small but non-negligible ferromagnetic moments observed in closed shell oxide systems, containing virtually no atoms with partially filled *d* or *f* shells. This intriguing ferromagnetism occurs even at temperatures well above room temperature and seems to exist outside the conventional *m*-*J* paradigm, where *m* and *J* represent the magnetic moment and the exchange coupling of electron spins, respectively. Thus far, the d<sup>0</sup> ferromagnetism has been observed almost universally in nanoscale oxides and is believed to result from magnetic moments related to a certain defective state. However, a simple defect-based model cannot account for the observed ferromagnetic behavior because of a rather localized nature of the relevant defect orbitals, which will be insufficient to induce long range ferromagnetic order, as has been shown by recent density functional theory (DFT) calculations including electronic correlation effects beyond standard (semilocal) DFT functionals.

As for the mechanism of d<sup>0</sup> ferromagnetism, we have recently shown from the DFT calculations on a series of MgO clusters that some crystallographically perfect nanocrystallites paradoxically result in nonstoichiometric compositions owing the finite number of constituting atoms, resulting in a spin-triplet ground state. On the basis of the calculations, we proposed an idea that ferromagnetism in nanoscale oxides can arise from the combined effect of crystal symmetry and inherent nonstoichiometry [1]. We believe that this idea is appealing in some ways, but this cannot give an answer as to how the localized defect states are linked and coupled, showing a collective ferromagnetic ordering.

When we say “defects” in oxides, we usually mean “atomic defects,” e.g., vacant atom sites, interstitial atoms, or substitution of a foreign atom for a normal one, in the bulk. Thus, previous theoretical calculations on defect-related ferromagnetism have been performed mainly on the atomic defects in the bulk using supercell methods. However, all the atoms at the surface can also be regarded as structural defects or imperfections because of the reduced number of coordination bonds. As for nanoscale oxides, the possible effect of these surface atoms may not be completely neglected. Furthermore, it has been demonstrated that the low-coordinated surface sites such as terraces, edges, and corners are more stable locations for atomic defects than the bulk sites because the formation energy of atomic defects will decrease with decreasing the number of surrounding atoms. This allows one to expect that these low-coordinated surface states could potentially contribute to the generation of defect-related ferromagnetism in nanoscale oxide, as suggested by recent observations. However, the possible surface effects on the defect related magnetism have not been well investigated theoretically.

We hence carry out a series of quantum chemical DFT calculations on isolated MgO clusters with surface

atomic defects, including O and Mg vacancies. Such isolated cluster models are not appropriate to investigate the electronic structure of the bulk system and the extended surface of crystals. When materials are reduced to the nanoscale, however, their structure and properties can deviate from the bulk or extended surface case. Accordingly, real space cluster models, rather than reciprocal space description, will become more effective in dealing especially with surface-related phenomena in nanocrystals.

## Methods

As for MgO clusters with more than ~50 atoms, it has been demonstrated that the cubic rock-salt structure thermodynamically dominates the energy landscape. We hence employed several top-down clusters based on cuts from the cubic rock-salt structure as representative models of nanometer-sized MgO crystals. We first consider a (4×4×4)-atom block of stoichiometric Mg<sub>32</sub>O<sub>32</sub> cluster consisting in total of 64 atoms. To evaluate the possible effect of location of the Mg (or O) vacancy site on the stable spin state we intentionally removed one Mg (or O) atom from a three-coordinated (corner), a five-coordinated (in-plane) or a six-coordinated (subsurface) site of the 4×4×4 cluster. We then performed full geometry optimization for the respective Mg-deficient (Mg<sub>31</sub>O<sub>32</sub>) and O-deficient (Mg<sub>32</sub>O<sub>31</sub>) clusters, starting from ideal cubic configurations, at the singlet (*S*=0) and triplet (*S*=1) spin states without imposing any structural constraints. As for the spin singlet calculations, we used a spin-restricted formalism. All the DFT calculations in this work were carried out using the gradient corrected Becke's three parameters hybrid exchange functional in combination with the correlation functional of Lee, Yang, and Parr (B3LYP) with the GAUSSIAN-09 code. It has previously been shown that such a hybrid DFT functional is useful to correct the self-interaction problem, which often leads to misleading conclusions with regards to hole localization and the resulting magnetic characteristics of the system. Mulliken's population analysis was conducted to calculate the spin densities of the clusters at B3LYP/6-31G(d) level. The stability of the resulting optimized clusters was evaluated in terms of the total energy along with the atomization energy (AE), which is defined as the energy necessary to dissociate the MgmOn cluster into neutral atoms (*m*Mg + *n*O), namely,  $AE = mE(\text{Mg}) + nE(\text{O}) - E(\text{Mg}_m\text{O}_n)$ , where  $E(X)$  represents the total energy of the system X. The AE is useful to evaluate the stability of the clusters with the same dimension but different compositions and spin states.

Furthermore, we employed a series of rocksalt-type clusters consisting of (4×4×4)-, (6×4×3)-, (7×4×3)-, and (8×4×3)-atom blocks to investigate whether the defect-induced spin polarization can couple ferromagnetically with each other. For that purpose we removed two corner Mg atoms located in the same (100) plane of the respective clusters, resulting in the Mg<sub>30</sub>O<sub>32</sub>, Mg<sub>34</sub>O<sub>36</sub>, Mg<sub>40</sub>O<sub>42</sub>, and Mg<sub>46</sub>O<sub>48</sub> clusters. Full geometry optimizations were performed as well for this series of Mg-deficient clusters at the B3LYP/6-31G(d) level by assuming that *S*=0, 1 and 2.

## Results and Discussion

First we show the results of the (4×4×4)-atom block of the clusters containing one Mg or one O vacancy. We found that irrespective of the assumed spin state, the starting cubic configuration is basically retained for all the clusters employed after full geometry optimization although a slight outward displacement of the atoms surrounding each vacancy site was seen. It should be noted, however, that the stability of the spin state varies

depending on the type and location of the defect included in the cluster (see Table I). Irrespective of the location of the vacancy, the lower energy spin state of the O-deficient ( $\text{Mg}_{32}\text{O}_{31}$ ) cluster is the singlet ( $S=0$ ) state. The cluster with a corner O vacancy in the singlet state results in the lowest energy state among the present series of  $\text{Mg}_{32}\text{O}_{31}$  clusters. This implies that the introduction of a surface O vacancy will not induce a spin polarized ground state, in agreement with the results deduced from previous supercell calculations. As for the Mg-deficient ( $\text{Mg}_{31}\text{O}_{32}$ ) cluster, however, the triplet ( $S=1$ ) state is always lower in total energy than the singlet ( $S=0$ ) state. The lowest energy state is the  $\text{Mg}_{31}\text{O}_{32}$  cluster with a corner Mg vacancy in the triplet state, which also yields the largest AE value among the clusters shown in Table I. Thus, the Mg-deficient cluster with an Mg vacancy at the corner can be regarded as the most stable defect configuration among the Mg- and O-deficient clusters investigated. Table I also reveal that for the Mg-deficient clusters the energy separation between the triplet and singlet states is  $\sim 1$  eV, showing substantial stability of the spin-polarized ground state. Such a large triplet-singlet energy gap has not been obtained for the Mg vacancy in the supercell-based model, where the triplet state is almost degenerate with the singlet state.

We next investigate the structure and spin states of the rocksalt-type clusters with two Mg vacancies at two end corners of the respective clusters. For that purpose we employed a series of clusters consisting of  $(4\times 4\times 4)$ -,  $(6\times 4\times 3)$ -,  $(7\times 4\times 3)$ -, and  $(8\times 4\times 3)$ -atom blocks. Similar to the case of the  $(4\times 4\times 4)$  cluster with one Mg vacancy, we found that the original cubic-like configuration is retained as well after geometry optimization. The inter-vacancy distances for the optimized  $(4\times 4\times 4)$ -,  $(6\times 4\times 3)$ -,  $(7\times 4\times 3)$ -, and  $(8\times 4\times 3)$  clusters are estimated to be  $\sim 8.5$ ,  $\sim 12.0$ ,  $\sim 12.5$ , and  $\sim 15.5$  Å, respectively, and the relative total energies of the spin-polarized ( $S=1$  and 2) states with respect to the spin-unpolarized closed-shell ( $S=0$ ) state are summarized in Table II.

One sees from Table II that all these Mg-deficient clusters are characterized by the same the energetic ordering of different spin states, namely,  $E_q < E_t < E_s$ , where  $E_q$ ,  $E_t$ , and  $E_s$  represent the total energy of the spin quintet, triplet and singlet states, respectively. The spin  $S=2$  and 0 states are separated by an energy of more than 1 eV, implying the existence of a stable spin-polarized state. Table II also shows that the spin triplet state is only

**Table I.** Electronic properties of the  $(4\times 4\times 4)$ -based MgO cluster with one Mg or one O vacancy at different sites. Geometry optimization was performed at the B3LYP/6-31G(d) level in the respective spin states.

cluster	spin state	$\Delta E^a$ (eV)	AE <sup>b</sup> (eV)	$\Delta E_{\text{H-L}}^c$ (eV)
$\text{Mg}_{32}\text{O}_{31}$				
corner O vacancy	singlet	–	270.588	1.68
	triplet	1.01	269.583	0.40 ( $\alpha$ )/3.38( $\beta$ )
in-plane O vacancy	singlet	–	269.258	1.68
	triplet	0.69	268.567	0.44( $\alpha$ )/3.58( $\beta$ )
subsurface O vacancy	singlet	–	268.684	1.59
	triplet <sup>d</sup>	–	–	–
$\text{Mg}_{31}\text{O}_{32}$				
corner Mg vacancy	singlet	–	269.409	0.47
	triplet	-1.303	270.712	3.97 ( $\alpha$ )/1.00 ( $\beta$ )
in-plane Mg vacancy	singlet	–	268.654	0.40
	triplet	-1.133	269.786	3.63 ( $\alpha$ )/1.25( $\beta$ )
subsurface Mg vacancy	singlet	–	268.495	0.49
	triplet	-0.985	269.480	3.89( $\alpha$ )/0.44( $\beta$ )

<sup>a</sup>  $\Delta E = E_{\text{triplet}} - E_{\text{singlet}}$ .  $E_{\text{triplet}}$  and  $E_{\text{singlet}}$  represent the total energy of the spin-triplet and spin-singlet states, respectively.

<sup>b</sup> AE (Atomization Energy) =  $mE(\text{Mg}) + nE(\text{O}) - E(\text{Mg}_m\text{O}_n)$ , where  $E(X)$  represents the total energy of the system  $X$ .

<sup>c</sup>  $\Delta E_{\text{H-L}}$  is the energy difference between the HOMO and the LUMO levels.  $\alpha$  and  $\beta$  indicate the major and minor spin states, respectively.

<sup>d</sup> The SCF did not converge for this cluster in the triplet state.

slightly higher in energy (several milli-electron volts) than the spin quintet state, suggesting the degeneracy of these two spin polarized states or the coexistence of ferromagnetic and antiferromagnetic coupling. We should note, however, that an unrestricted DFT (UDFT) single determinant is not an eigenfunction of the total spin operator  $S^2$  and inherently has the spin impurity problem. One sees from Table II that the spin-squared expectation values  $\langle S^2 \rangle$  for the spin quintet ( $S=2$ ) state are around 6.02–6.03, which is close to the ideal value  $S(S+1)=6$ , even before annihilation of the first spin contaminant. In the case of the triplet state, however, the  $\langle S^2 \rangle$  values are  $\sim 3.02$  and  $\sim 2.05$  before and after annihilation of the first spin contaminant, respectively. This indicates that the calculation for the triplet state is affected by mixing with a higher spin (possibly quintet) state.

**Table II.** Electronic properties of various MgO-type clusters with two corner Mg vacancies optimized at the B3LYP/6-31G(d) level in the respective spin states.

cluster	spin state	$\Delta E^a$ (eV)	AE <sup>b</sup> (eV)	$\langle S^2 \rangle^c$	$\Delta E_{H-L}^d$ (eV)
Mg <sub>30</sub> O <sub>32</sub> (4×4×4)	singlet	–	261.701	0	0.46
	triplet	–1.354	263.055	3.026 (2.055)	1.65 (α)/1.20(β)
	quintet	–1.362	293.063	6.028 (6.000)	4.20 (α)/1.18(β)
Mg <sub>34</sub> O <sub>36</sub> (6×4×3)	singlet	–	295.868	0	0.59
	triplet	–2.679	298.547	3.020 (2.045)	1.34 (α)/1.31(β)
	quintet	–2.682	298.550	6.023 (6.000)	4.36 (α)/1.22(β)
Mg <sub>40</sub> O <sub>42</sub> (7×4×3)	singlet	–	350.281	0	0.64
	triplet	–2.669	352.950	3.024 (2.045)	1.41 (α)/1.40(β)
	quintet	–2.673	352.954	6.024 (6.000)	4.36 (α)/1.39(β)
Mg <sub>46</sub> O <sub>48</sub> (8×4×3)	singlet	–	404.873	0	0.64
	triplet	–2.687	407.560	3.024 (2.049)	1.80 (α)/1.43(β)
	quintet	–2.690	407.563	6.024 (6.000)	4.35 (α)/1.43(β)

<sup>a</sup>Triplet or quintet state energy minus closed-shell singlet state energy. <sup>b</sup>AE (Atomization Energy) =  $mE(\text{Mg}) + nE(\text{O}) - E(\text{Mg}_m\text{O}_n)$ , where  $E(X)$  represents the total energy of the system  $X$ . <sup>c</sup>The values in parentheses are those after annihilation of the first spin contaminant. <sup>d</sup> $E_{H-L}$  is the energy difference between the HOMO and the LUMO levels.  $\alpha$  and  $\beta$  indicate the major and minor spin states, respectively.

## Conclusions

We have investigated the effect of surface defects and the related low-coordinated surface atoms on the defect-induced magnetism in MgO nanocrystallites using hybrid density functional theory calculations. It has been demonstrated that when Mg vacancies are introduced at the surface or near surface of cube-like MgO clusters, a magnetic state becomes lower in total energy than the nonmagnetic singlet state by several electron volts, resulting in the robust spin-polarized ground state. The total spin  $S$  of the clusters in their ground state is equal to the number of the surface Mg vacancies introduced. The resulting spin density is not only located at the surrounding O atoms neighbor to the Mg vacancy site but is also extended to the low-coordinated surface O atoms along the  $\langle 110 \rangle$  direction. This directional spin delocalization allows a remote ( $\sim 1$  nm or longer) vacancy-vacancy interaction, eventually leading to a long-range ferromagnetic interaction.

## 発表論文

T. Uchino and T. Yoko, “Symmetry and Nonstoichiometry as Possible Origins of Ferromagnetism in Nanoscale Oxides,” *Phys. Rev. B* **85**, 012407-1-5 (2012).

## 参考論文

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