ガラスの構造研究

Study on the Structure of Glass

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Introduction

We investigate 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 (S=0) by several electron volts, resulting in the robust spin-polarized ground state [1]. 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 <110> direction. This directional spin delocalization allows a remote (~1 nm or longer) vacancy-vacancy interaction, eventually leading to a long-range ferromagnetic interaction.

Methods

We here 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 $Mg_{32}O_{32}$ cluster consisting in total of 64 atoms, as shown in Fig. 1(a). To evaluate the effect of a surface Mg (or O) vacancy on the stable spin state we intentionally removed one Mg (or O) atom at one of the corner sites of the 4×4×4 cluster. We then performed full geometry optimization for

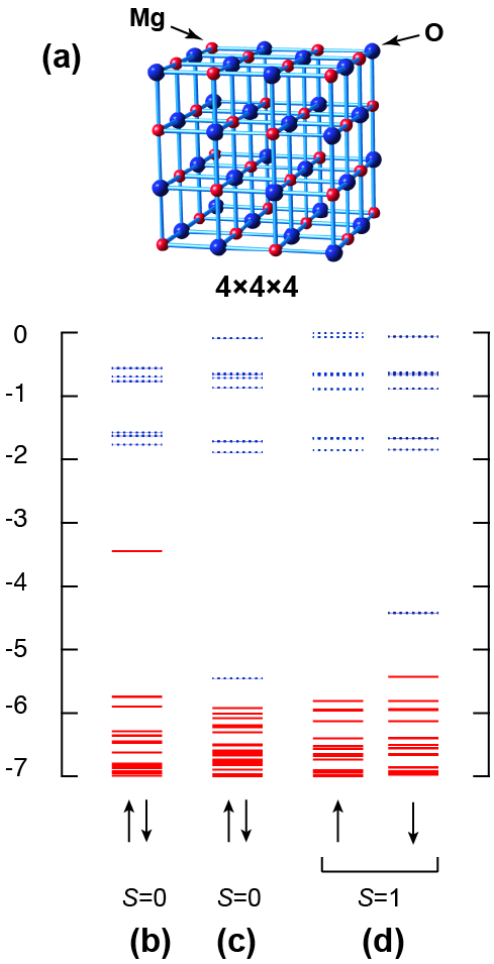

Figure 1. (a) A (4×4×4)-atom block of the $Mg_{32}O_{32}$ cluster. A corner Mg (or O) atom, indicated by an arrow, is removed to create an Mg-(or O-) deficient cluster. Molecular orbital energy-level diagrams of occupied molecular orbitals (solid lines) and unoccupied molecular orbitals (dotted lines) calculated for (b) the O-deficient Mg32O31 cluster in the spin-singlet state, (c) the Mg-deficient $Mg_{31}O_{32}$ cluster in the spin-singlet state, (d) the Mg-deficient $Mg_{31}O_{32}$ cluster in the spin-triplet state.

these Mg-deficient ($Mg_{31}O_{32}$) and O-deficient ($Mg_{32}O_{31}$) clusters, starting from ideal cubic configurations, at the spin-restricted singlet (S=0) and spin-unrestricted triplet (S=1) spin states without imposing any structural constraints. 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. Mulliken's population analysis was conducted to calculate the spin densities of the clusters at B3LYP/6-31G(d) level.

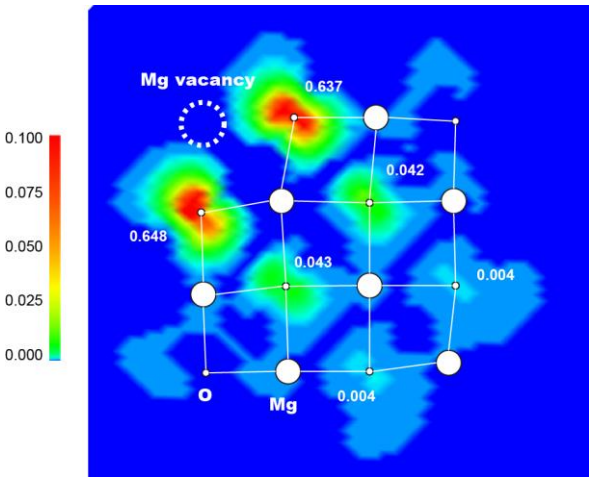

Figure 2. Spin density map on one of the (100) planes for the $Mg_{31}O_{32}$ cluster in the spin-triplet state. Large and small circles represent Mg and O atoms, respectively. The values indicated are Mulliken atomic spin densities; the values below 0.001 are omitted.

Results and Discussion

We found that irrespective of the assumed spin state, the starting cubic configuration is almost retained for all the clusters employed after full geometry optimization although slight outward atomic displacements with respect to the respective vacancy sites were seen. It should be noted, however, that the stability of the spin state varies depending on the type of defect included in the cluster. The lower energy spin state of the O-deficient ($Mg_{32}O_{31}$) cluster is the singlet (S=0) state, in agreement with the results of supercell calculations. As for the Mg-deficient ($Mg_{31}O_{32}$) cluster, however, the triplet (S=1) state is substantially lower in total energy than the singlet (S=0) state by ~1.3 eV. 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 generally almost degenerate with the singlet state.

The spin-polarized ground state of the Mg-deficient cluster can be interpreted in terms of the molecular orbital diagrams shown in Fig. 1. As for the Mg-deficient cluster in the singlet state, the lowest unoccupied molecular orbital (LUMO), which is characterized basically by 2p orbitals of O atoms, is only slightly higher in energy than the highest occupied molecular orbital (HOMO) by ~0.5 eV [see Fig. 1(c)]. This contrasts with the case of the O-deficient cluster in the singlet state, where the LUMO is higher in energy than the HOMO by ~1.7 eV [see Fig. 1(b)]. It hence follows that spontaneous spin polarization is expected to occur in the Mg-deficient cluster because of a small HOMO-LUMO gap, which costs less energy to flip a spin, leading to the spin polarized ground state [see Fig. 1(d)].

We next investigate the spin-magnetization density, which is defined as the local density difference between the spin-up and spin-down states, of the Mg-deficient cluster in the triplet state (see Fig. 2). One sees from Fig. 2 that most of the spin is distributed over the oxygen atoms adjacent to the corner Mg vacancy. This feature is basically in agreement with that calculated previously for the Mg vacancy introduced into an MgO supercell. In the present Mg-deficient cluster, however, a non-negligible spin density is further spread out of the nearest

neighbor oxygen atoms along the <110> directions on the {100} surfaces. We also found that the value of the Mulliken atomic spin density of the surface Mg and subsurface O and Mg atoms are below 0.0005, indicating that the defect derived spin density is preferentially distributed over the low-coordinated surface O atoms.

Conclusions

we have shown from a series of DFT calculations on MgO nanoclusters that a Mg corner vacancy can induce a delocalized spin distribution over several neighboring surface O atoms along the <110> directions. This directional spin delocalization enables a pair of distant (~1 nm or longer) Mg vacancies to interact ferromagnetically, resulting in the spin polarized ground state. These results allow us to suggest that the low-coordinated surface atoms are prerequisite for long-range ferromagnetic interaction, hence providing a delocalized mediating state or a percolation network for defect-related ferromagnetism in nanoscale oxides.

発表論文

T. Uchino and T. Yoko, “Spin-polarized ground states and ferromagnetic order induced by low-coordinated surface atoms and defects in nanoscale magnesium oxide,” *Phys. Rev. B* **87**, 144414 (2013).

参考論文

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