Chemically Induced Oscillatory Exchange Coupling in Chromium Oxide Clusters

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Theoretical electronic structure studies of the ground state geometries, binding energies, and magnetic coupling of Cr_2O_n ($n = 1-6$) clusters have been carried out within a density functional scheme. It is shown that the magnetic coupling of the Cr atoms oscillates from antiferromagnetic to ferromagnetic and back as O atoms are added. Detailed electronic structure analysis reveals that the oscillatory exchange coupling has a chemical origin and is induced by changes in the electronic states between Cr and O sites close to the Fermi energy.

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One of the most exciting phenomena in magnetism is the possibility of an oscillatory exchange coupling. The notable examples are the RKKY interaction and the oscillatory exchange coupling between ultrathin ferromagnetic layers separated by ultrathin nonferromagnetic interlayers as observed in the Fe-Cr system [1]. In the RKKY, the interaction between localized moments is mediated by the conduction electrons and oscillates as a function of distance with a period determined by the Fermi wave number of the electron gas. In the multilayers, the exchange coupling between ferromagnetic layers (e.g., Fe) oscillates with the thickness of the nonmagnetic layer (e.g., Cr). Here we show a new kind of oscillatory exchange interaction where the coupling between magnetic atoms of an otherwise nonmagnetic solid oscillates due to changes in the chemical bonding. We show that the coupling between two Cr atoms in Cr_2O_n clusters oscillates as the number of oxygen atoms is varied. A detailed electronic structure analysis reveals that the oscillations are a direct consequence of the changes in the electronic states between Cr and O atoms in the vicinity of Fermi energy.

In bulk, Cr forms binary oxides CrO_2 and Cr_2O_3. CrO_2, widely used in magnetic recording tapes, has a rutile structure in the bulk. The Cr atoms form a body-centered tetragonal lattice and each Cr is surrounded by an oxygen octahedron which is rotated as one goes from the central to the corner Cr site of the body-centered cube of Cr atoms. The solid is metallic and ferromagnetic. This is unusual since oxides are generally nonmetallic and antiferromagnetic or ferrimagnetic as the magnetic coupling is marked by strong antiferromagnetic contribution. The unusual behavior of CrO_2 has been the subject of intense research [2,3]. It is proposed [2] that the Cr *d* bands are divided into two sets: a localized and weakly interacting *d* state providing the local atomic moments and a set of strongly hybridized *d* states close to the Fermi energy leading to the metallic character. The ferromagnetism in CrO_2 is therefore due to localized states and is different from the conventional band ferromagnetism. The unusual behavior of oxides is further seen as one goes to the other chromium oxygen compound, namely, Cr_2O_3. In contrast to CrO_2, solid Cr_2O_3 [4] has a corundum structure and is an antiferromagnetic insulator. This indicates that the electronic character and the magnetic interaction between Cr moments can be significantly altered by changing the ratio between Cr and O atoms. The solid compounds exist only for a specific ratio of the constituents. However, small clusters containing Cr and O can be formed over a wide range of compositions and offer an ideal system to investigate such progressions of electronic and magnetic behaviors.

In this Letter we present results of detailed electronic structure investigations on Cr_2O_n clusters containing $n = 1-6$ oxygen atoms. Our ground state geometries are in agreement with recently proposed structures of Cr_2O_n ($n = 2-4$) clusters based on infrared spectroscopy [5]. The main focus of the current work, however, is the magnetic behavior. We show that the local magnetic moment at the Cr sites decreases as the O content is increased. What is surprising is that the change in moment is accompanied by a change in magnetic coupling. The Cr atoms in clusters containing one and two oxygen atoms are antiferromagnetically coupled as in a free Cr_2 dimer. However, the Cr sites in Cr_2O_3, composition at which the solid is an antiferromagnetic insulator, become ferromagnetically coupled. A further increase in O content to form Cr_2O_4 results in the reappearance of the antiferromagnetic coupling. Finally the Cr sites in Cr_2O_5 and Cr_2O_6 have negligible local moments. A detailed electronic structure analysis reveals that the electronic structure is marked by localized Cr states below the Fermi energy and strongly hybridized Cr *d* and O *p* states close to the Fermi energy. The successive addition of O atoms results in enhanced mixing between localized and delocalized Cr states and the oxygen *p* states. While the former leads to a decrease of the Cr moment, the latter affects the nature of the magnetic coupling.

The theoretical studies were carried out using a linear combination of the atomic orbital/molecular orbital approach within the density functional formalism. The implementation used by us is called the DMOL software [6] and is based on the discrete variational method proposed originally by Ellis and co-workers [7]. Here, the molecular orbitals are expressed as a linear combination of atomic orbitals centered at the atomic sites and taken in a numerical form. The Hamiltonian matrix elements entering the Kohn-Sham equation [8] are calculated via numerical integration over a mesh of points. The basis set for Cr had $3s$, $3p$, $3d$, and $4s$ orbitals and the $4p$ polarization functions. For O, the basis set had $2s$, $2p$ orbitals. The inner cores were frozen. The exchange correlation effects were included via a local spin density functional [9] and the effect of gradient corrections [10] was studied. We found that the inclusion of gradient corrections had no qualitative effect on the results. However, the inclusion of gradient corrections for a Cr_2 molecule leads to an abnormally large bond length compared to experiment while the local density leads to a correct bond length. In view of these results, we report here only results based on local density approximation. The above choice of basis leads to reasonable estimates of the ionization potential of atoms and these comparisons will be reported in a detailed paper.

The ground state of a free Cr_2 cluster is an antiferromagnetic configuration with local moments of $2.6\mu_B$. The molecule had a bond length of 1.70 Å and a binding energy of 2.28 eV compared to the corresponding experimental [11,12] values of 1.68 Å and 1.42 eV, respectively. While the bond length is in good agreement with experiment, the binding energy is overestimated. The overestimation of the binding energy in local density approximation is well known. For a more detailed comparison of our results on Cr_2 with previous studies and experiment, the reader is referred to our recent paper [13].

Before we discuss the electronic and magnetic structures of Cr_2O_n clusters, it is instructive to have a general idea about the effect of O on Cr. To this end, we calculated a CrO molecule. It had a binding energy of 6.15 eV and a bond length of 1.60 Å compared to experimental values of 4.3 eV and 1.61 Å, respectively [11]. The molecule had four unpaired spins in agreement with experimental spin multiplicity [11]. A Mulliken population analysis showed that the Cr and O sites have local moments of $4.17\mu_B$ and $-0.17\mu_B$, respectively. Noting that an isolated Cr atom has six unpaired spins, the effect of adding oxygen is to reduce the local moment at the Cr site.

We now discuss the ground states of Cr_2O_n clusters. For each cluster, several geometries were examined and in each case the structure was optimized by moving atoms in the direction of forces. Most of the clusters were marked by several energetically close multiplets. The ground state determination therefore also involved optimization of the spin multiplicity. As mentioned above, the main focus of the present work is the investigation of magnetic structures which involves investigations of antiferromagnetic arrangements. These calculations required breaking of the overall spatial symmetry. The symmetries mentioned in the following to describe the geometries are only to give an idea about the geometrical parameters varied to determine the ground state. In the full Hamiltonian, however, the symmetry was broken for the antiferromagnetic structures.

Figure 1 shows the ground state geometries of the various Cr_2O_n clusters. For Cr_2O, the ground state is a C_{2v} structure with a binding energy of 8.96 eV. For Cr_2O_2, we tried a rhombus C_{2v} and an open structure. The ground state corresponds to the closed structure and had a binding energy of 16.58 eV. For Cr_2O_3, the ground state corresponds to a Cr_2O_2 with an additional O atom attached to a Cr site. It had a binding energy of 24.0 eV. The ground state of Cr_2O_4 can be described as Cr_2O_2 with two O atoms attached to two Cr atoms. It had a binding energy of 31.67 eV. Cr_2O_5 and Cr_2O_6 are extensions of Cr_2O_4 with additional O atoms attached to Cr atoms. They had binding energies of 38.39 eV and 44.82 eV, respectively. It is interesting to note that all the geometries in Fig. 1 can be considered as fragments of the bulk CrO_2 structure.

As mentioned earlier, Chertihin *et al.* [5] investigated structures of Cr_2O_n ($n = 2-4$) using infrared spectroscopy. For Cr_2O_2, they have identified a chainlike and a ringlike structure. We find the ring to be slightly more stable than the chain. For Cr_2O_3, their experiments suggest a puckered ring with a terminal oxygen as obtained by us. The IR experiments on Cr_2O_4 suggest a configuration with two nonequivalent O atoms which is consistent with the structure obtained above. We would like to add that Xiang *et al.* [14] also recently carried out some calculations on small chromium oxide clusters and our geometries for Cr_2O_m ($m = 2-4$) are similar to their results. These authors, however, did not investigate the antiferromagnetic states.

The key focus of the present work is the magnetic structure. For all the clusters, we carried out a Mulliken population analysis to determine the local magnetic moment at

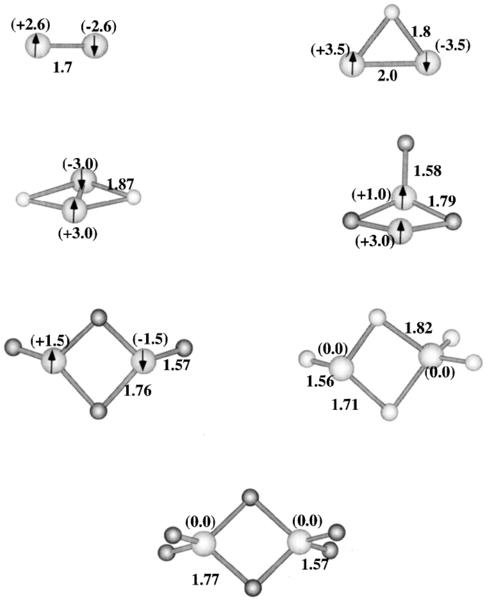

FIG. 1. Ground state geometries of Cr_2O_n ($n = 1-6$) clusters. The bigger atoms are Cr atoms while the smaller are O atoms. The bond lengths are in Å. The magnetic moments in μ_B at the Cr sites are marked within the parentheses.

the various sites. These are marked within parentheses in Fig. 1. The ground state of Cr_2O_2 has a multiplicity of 1 and, as shown in Fig. 1, the moments at the Cr sites have values of $+3.0\mu_B$ and $-3.0\mu_B$ and are antiferromagnetically coupled. The addition of an O atom to form Cr_2O_3 results in a Cr site with two oxygen bonds and this Cr undergoes a substantial reduction in moment. The cluster has a multiplicity of 5. Surprisingly, the moments at the two Cr sites are ferromagnetically coupled. The addition of an O atom to form Cr_2O_4 now results in the additional O bound to the other Cr atom and now the two Cr sites are again antiferromagnetically coupled. Finally, in Cr_2O_5 or Cr_2O_6, the Cr sites have negligible moments.

In addition to the ground state, we examined the energy required to change the magnetic coupling of a given cluster. This required calculation of the excited antiferromagnetic (ferromagnetic) state for the ferromagnetic (antiferromagnetic) ground state. In Fig. 2 we plot the energy difference between the lowest ferromagnetic and antiferromagnetic states for all the clusters. Note that the difference energy which is a measure of the exchange coupling oscillates as a function of size.

The above results show that the successive addition of O atoms to form Cr_2O_n clusters leads to a reduction of the localized moment at the Cr sites and an oscillation of the magnetic coupling. Both these variations can be related to the progression in the chemical bonding between the Cr and O of which the basic features can be illustrated by analyzing the bonding in a CrO molecule. Figure 3 shows the one electron levels in a free Cr atom and an O atom and the molecular levels in a CrO molecule. Only $3d$ and $4s$ levels on Cr and the $2p$ levels on O are shown (the filled $3s$ and $3p$ levels on Cr and the $2s$ levels on O are relatively deep and are not shown). An isolated Cr atom has six unpaired electrons while the O $2p$ level has two unpaired electrons (three majority and one minority electrons). The isolated atoms therefore have eight unpaired spins. As the atoms are brought together to form a molecule, the mixing between the Cr d states and the O p states leads to covalent pd hybrid states. For the minority spin, the unfilled minority p states of the O atom mix with the $d_{3z^2-r^2}$, d_{xz}, and d_{yz} states assuming that the O atom is located along the z axis. The relative position of levels is such that the bonding hybrids for minority spin lie below the Fermi energy and become occupied in the molecule. The overall number of unpaired spins is therefore reduced by 4 and the resulting molecule has only four unpaired spins. The effect of bonding is thus to induce opposite spin polarization at the Cr sites by forming minority orbitals lying below the Fermi energy. As one goes to larger clusters, the situation becomes more complicated since the changes in symmetry now also permit mixing between Cr d_{xy} and $d_{x^2-y^2}$ and the O p states. The net effect is, however, to induce minority spin states at the Cr site. If the initial Cr moment is large this leads to a reduction of moment at the Cr site, but around Cr_2O_2 the Cr moment is sufficiently

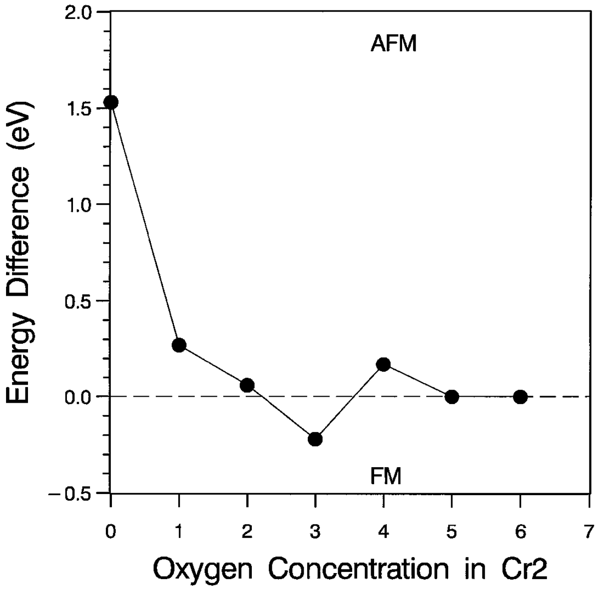

FIG. 2. Energy difference between the ferromagnetic and the antiferromagnetic states as a function of cluster size for various clusters. The positive values indicate a ferromagnetic ground state whereas the negative values indicate an antiferromagnetic ground state.

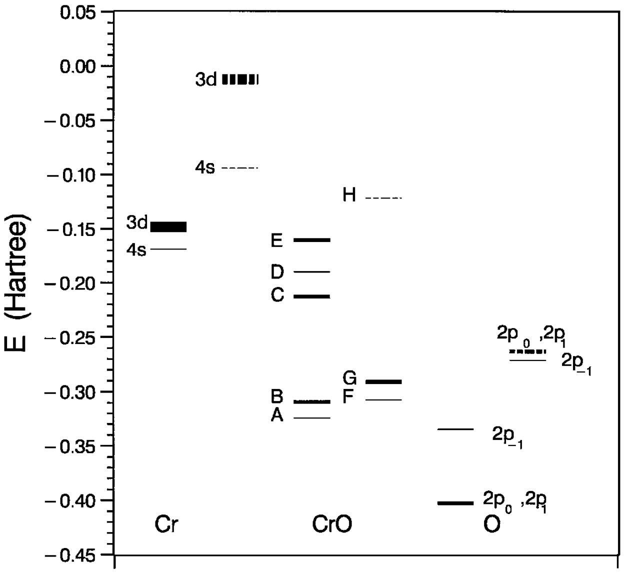

FIG. 3. One electron levels in Cr, O, and CrO. Level A has contributions from $3d_0$ on Cr and the $2s + 2p_0$ states of O. Two degenerate levels B have contributions from $3d_{-1}$ of Cr and $2p_{-1}$ of O, and from $3d_1$ of Cr and $2p_1$ of O, respectively. The two degenerate C levels are the $3d_{-2}$ and $3d_2$ levels of Cr. Level D has contributions from the $4s$ and $3d^0$ states of Cr and the $2p^0$ state of O. The two degenerate E levels contain only one electron and have contributions from $3d_{-1}$ of Cr and $2p_{-1}$ of O and $3d_1$ of Cr and $2p_1$ of O, respectively. Level F has contributions from $3d_0$ of Cr and $2s + 2p_0$ of O. Degenerate levels G are made up of $3d_{-1} + 3d_1$ of Cr and $2p_{-1} + 2p_1$ of O. Level H has contributions from the $4s$ state of Cr and the $3d_0$ state of O.

reduced so that the bonding to an O atom to the minority Cr orbitals adds sufficient opposite polarization and results in a reversal of the local moment. Starting from Cr_2O_2 which has antiferromagnetically coupled Cr sites, the addition of O then leads to ferromagnetically coupled moments since the polarization of the Cr site attached to additional O changes sign. In this case, the O sites linking the two Cr atoms are antiferromagnetically coupled to the Cr sites with a local moment of $0.08\mu_B$. Further addition of an O atom to Cr_2O_3 can produce two effects. If the additional O is attached to the Cr which has triple coordination to O, the O further enhances the opposite moment of the previous O and the two Cr remain ferromagnetically coupled. On the other hand, when the O is attached to other Cr which lack a number of O bonds, the O induces an opposite moment and the two Cr again become antiferromagnetically coupled. The energetics show that the latter situation is more stable and therefore a Cr_2O_4 has antiferromagnetically coupled Cr atoms in its ground state. These considerations illustrate that it is the coupling between Cr and O which is responsible for the observed effect.

It is interesting to compare the behavior in clusters to that in bulk. As pointed out above, bulk CrO_2 is a half-metallic ferromagnet while bulk Cr_2O_3 is an antiferromagnetic insulator. In case of clusters, Cr_2O_4, which has the same composition as CrO_2, has antiferromagnetically coupled while a Cr_2O_3 cluster has ferromagnetically coupled Cr sites. Bulk Cr_2O_3 has a corundum structure which can be described as a hexagonal closed packing of O atoms with two-thirds of the octahedric sites occupied by Cr. We found that a triangular bipyramid Cr_2O_3 cluster with a triangular base of O atoms capped by two Cr sites resembling the solid does favor antiferromagnetically aligned Cr sites. The ground state (Fig. 1), however, is a structure where one of the Cr sites has an additional O bond and this, as discussed above, favors the ferromagnetic alignment. In a Cr_2O_4 cluster, on the other hand, the bonding is very different from the bulk CrO_2 where the localized component of d states provides the local magnetic moment while the nonlocalized component mixing strongly with oxygen band leads to a half-metallic ferromagnet. In clusters, which have incomplete oxygen octahedron around Cr sites, the magnetic coupling is different from the bulk.

To summarize, we have demonstrated an oscillatory exchange coupling which is rooted in the chemical bonding between Cr and O. We have shown that the combination of size, geometry, and the localized states make clusters very different from the bulk. We would like to add that while the present studies are done on Cr_2O_n clusters the basic ideas are general and are applicable to larger clusters and may provide a new way of controlling the magnetic interactions in small clusters via chemical reactions.

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[1] P. Grunberg, R. Schreiber, Y. Pang, M. B. Brodsky, and H. Sowers, Phys. Rev. Lett. **57**, 2442 (1986).

[2] M. A. Korotin, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. Lett. **80**, 4305 (1998).

[3] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[4] *Transition Metal Oxides,* edited by C. N. R. Rao and B. Raveau (Wiley-VCH, New York, 1998).

[5] G. V. Chertihin, W. D. Bare, and L. Andrews, J. Chem. Phys. **107**, 2798 (1997).

[6] DMOL, version 950, Molecular Simulations Inc., 1995.

[7] D. E. Ellis, Int. J. Quantum Chem. **S2**, 35 (1968).

[8] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[9] S. H. Vosko, L. Wilk, and M. Nusair, J. Can. Phys. **58**, 1200 (1980).

[10] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[11] *Constants of Diatomic Molecules,* Molecular Spectra and Molecular Structure Vol. IV, edited by K. P. Huber and G. Herzberg (Van Nostrand Reinhold, New York, 1974).

[12] C.-X. Su and P. B. Armentrout, J. Chem. Phys. **99**, 6506 (1993).

[13] N. Desmarais, F. A. Reuse, B. V. Reddy, and S. N. Khanna (to be published).

[14] K. Xiang, R. Pandey, J. M. Recio, F. Francisco, and J. M. Newsam (private communication).