Dimer Growth, Structural Transition, and Antiferromagnetic Ordering of Small Chromium Clusters

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The evolution of structural and magnetic properties of small chromium clusters towards the bulk is elucidated through a systematic density functional study. A tightly bound Cr_2 dimer is found to play a key role in determining the cluster structures. A unique dimer growth route is discovered for clusters up to Cr_{11}, at which a structural transition occurs from the dimer growth to a bulklike body-centered-cubic structure. All the clusters exhibit antiferromagnetic ordering with size-dependent magnetic moments.   [S0031-9007(96)00507-8]

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Unraveling the structural evolution and physicochemical properties of transition metal clusters is of both fundamental and technological importance and has presented a considerable challenge in cluster science. Chromium is unique among the transition metals. Its $3d^5 4s^1$ half-filled electronic configuration results in strong d-d bonding in the dimer with an exceptionally short bond length (1.68 Å) [1–4], while bulk chromium is antiferromagnetic with a body-centered-cubic (bcc) structure (nearest Cr-Cr distance: 2.50 Å) [5]. Two issues arise in understanding chromium clusters: (1) the evolution from a tightly bonded dimer towards the bulk structure and (2) the cluster magnetism. Using *ab initio* density functional theory, we carried out a systematic study on chromium clusters up to Cr_{15}. Exhaustive structural search was performed by fully optimizing the cluster geometries with a variety of atomic configurations. We observed a dimer-growth route that gives rise to even-odd alternations of some key physical properties for clusters up to Cr_{11}. A structural transition occurs at Cr_{11} from the dimer growth to bcc-like structures, and the clusters start resembling the bulk. All the clusters are found to be antiferromagnetically coupled with size-dependent magnetic moments. The present study represents a significant progress towards completely understanding the complex nature of the structural and electronic properties of the transition metal clusters.

All calculations were performed using the local spin density functional approximation (LSD) provided by the DMOL package [6,7]. The Cr $1s2s2p$ electrons were frozen to simplify the computation without significantly sacrificing the accuracy. We employed the Vosko-Wilk-Nusair local correlation functional together with the double numerical basis set augmented by polarization functions [8]. The quality of the present LSD calculation is demonstrated by the good agreement between the calculated dimer bond length (1.69 Å) and the experimental value (1.68 Å) [3]. An angular momentum number one greater than the maximum angular momentum number in the atomic orbital basis was used to specify the multipolar fitting that describe the analytical forms of the charge density and the Coulombic potential [7]. A charge smear function was applied in a self-consistent manner to enhance the self-consistent field (SCF) convergence. From Cr_3 to Cr_{12}, we performed an exhaustive structural search by fully optimizing the cluster geometries without imposing symmetry constraints for a wide variety of trial structures. For Cr_{13} to Cr_{15}, point group symmetries were imposed in our geometry optimization to confine the cluster structures to the bcc-like framework.

The electronic configuration of the chromium dimer plays a key role in determining the structures of small chromium clusters [9]. Cr_2 is a closed-shell system with a sextuple bond. The bonding orbitals formed by the $3d$ orbitals of chromium are completely filled. This unique electronic configuration results in a strong $3d$-$3d$ interaction and an unusually short dimer bond length, forcing the $4s$-$4s$ interaction into a slightly repulsive regime due to Pauli exclusion. It would therefore require strong orbital interactions to "unlock" the d electrons from the dimer molecular orbitals. Such an electronic structure is expected to be very stable. Indeed, our calculations show that Cr_3 is basically composed of a dimer plus an atom: The dimer electronic structure in Cr_3 is hardly changed with the third atom essentially remaining in its atomic electronic state, leaving six unpaired electrons in the cluster. In Cr_4, the fourth atom pairs up with the third atom in Cr_3, forming a weakly bonded dimer-dimer structure. The calculated electron density maps of Cr_2–Cr_4 are shown in Fig. 1. The electron density maps of Cr_5–Cr_{11} exhibit similar features: dimers and isolated atoms are surrounded with high electron density with little density in between. It is clear that the exceptionally strong $3d$-$3d$ interactions in the dimer dictate the growth and structure of the small Cr clusters.

The fully optimized cluster structures for Cr_2–Cr_{15} are displayed in Fig. 2. The arrows represent the directions
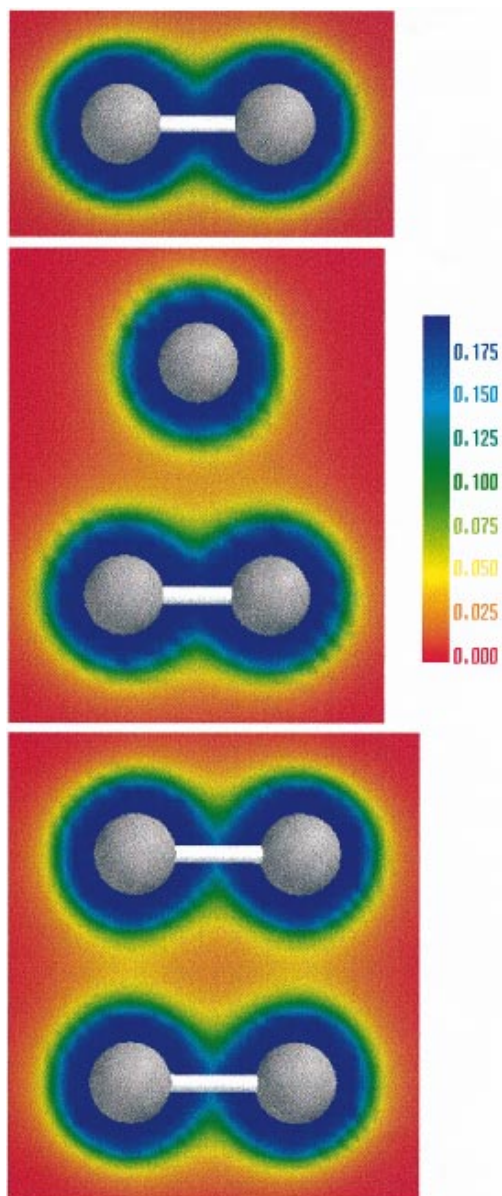
FIG. 1(color). The calculated electron density maps of Cr_2, Cr_3, and Cr_4. They illustrate that the electron density is mainly concentrated in between the two nuclei in Cr_2, is divided between the dimer and the third atom in Cr_3, and is well separated between the two dimers in Cr_4. The dimer stability is primarily due to the strong $3d$-$3d$ interaction, resulting in a closed-shell electronic configuration. The role of the strong dimer bonding is clearly seen in Cr_3 and Cr_4. In Cr_3, there are six unpaired electrons localized entirely in the unperturbed $3d$ orbitals and the slightly perturbed $4s$ orbital of the third atom. Cr_4 consists of two closed-shell dimers with relatively weak interdimer overlap between the σ_{4s}-σ_{4s} orbitals and between the $3d$-$3d$ orbitals. The electron density maps for Cr_5–Cr_{11} exhibit similar features except being three dimensional.

of local atomic spins and the dark bonds highlight the dimerlike bonds. The structures shown here represent the most energetically favorable ones. A dimer-growth route is clearly seen for clusters up to Cr_{11}, beyond which

bcc-like structures prevail. The even clusters up to Cr_8 are simply made of dimers stacking together, while the odd clusters up to Cr_9 consist of dimers and an isolated atom bonded to the adjacent dimers. Table I lists the calculated binding energies for all the clusters. For Cr_3–Cr_5, other isomers are also included [10]. A particularly interesting cluster is Cr_5 in which the two dimers are shifted from a perfect rectangle (Fig. 2). The isolated atom is apparently unable to unlock the strong electron pairing in the dimers, only causing the dimers to slide against each other. The dimer-sliding effect is expected due to the relatively weak interdimer interactions. In fact, our extensive structural search showed that dimer sliding also occurs in several other small chromium clusters. For example, the energy of a rhombus structure for Cr_4 was found to be comparable to that of the D_{2h} rectangle (Table I); a D_{2h} isomer of Cr_8 has stability similar to the one shown in Fig. 2. Significantly, the dimer growth is interrupted starting at Cr_{10}, which possesses only four dimerlike bonds with two isolated atoms [11]. The structure of Cr_{10} represents the first deviation from the dimer-growth route. Cr_{11} further deviates from the dimer growth and leads to a natural transition from the simple dimer stacks to a bcc-like structure: It possesses four dimerlike bonds and, at the same time, is the smallest cluster where the bcc-like structure with a central atom is energetically more favorable. From Cr_{12} and up, the bulklike bcc structures dominate the cluster growth and no dimerlike bonds can be identified in the minimum energy structures.

For clusters smaller than Cr_{11}, the dimerlike bonds do not exceed 2.0 Å. The relatively weak interactions among dimers or between dimers and isolated atoms result in the longer bonds. These weak interactions are also responsible for the range of dimer bond lengths. For example, in Cr_3 the dimerlike bond becomes shorter due to the σ_{4s}-$4s$ orbital overlap between the dimer and the third atom, resulting in a slight shift of the σ_{4s} electron density towards the third atom (Fig. 1). In Cr_4, however, the dimer-dimer interaction includes both interdimer σ_{4s}-σ_{4s} and $3d$-$3d$ overlaps, yielding a slight stretch to the dimer bonds. Clearly, the cluster structures are governed by both interdimer and intradimer interactions. For smaller clusters, the intradimer interaction dominates, resulting in the dimer-growth route. The interdimer interaction becomes stronger as cluster size increases, leading to the ultimate structural transition from the dimer growth to the bcc-like structures. For clusters larger than Cr_{11}, though dimerlike bonds no longer exist, the bond lengths are, in general, still more contracted than those in the bulk to maximize the orbital overlaps, as expected.

The immediate consequence of the dimer-growth structures is that there should be observable differences in properties between the even and odd clusters. Indeed, even-odd alternation has been observed for small Cr clusters in at least two experiments, providing direct supports
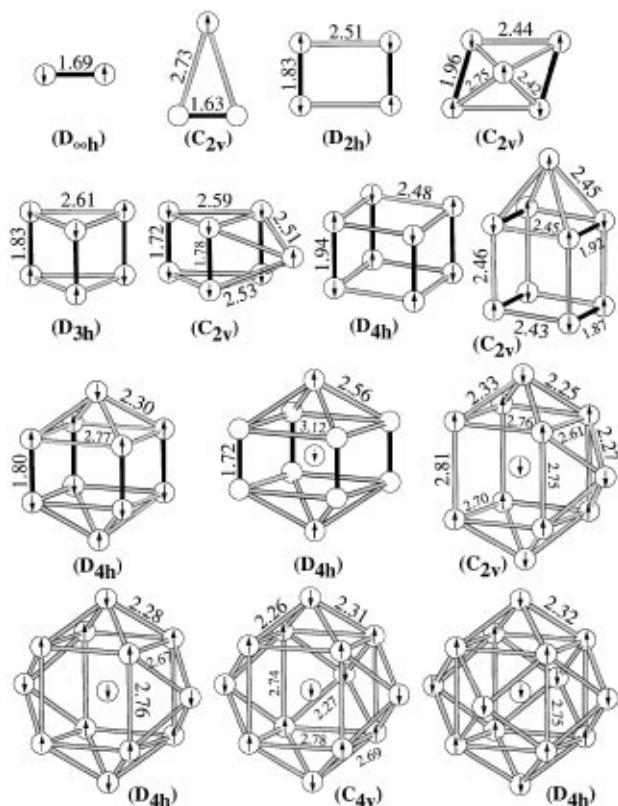
FIG. 2. Fully optimized Cr cluster structures. The bond lengths are in Å, and the arrows indicate the directions of the local atomic spins. No arrows are shown for the dimer atoms in Cr_3 and Cr_{11} because they possess negligible local moments. The structures shown here represent the most energetically favorable ones. The average magnetic moment for each cluster in μ_B/atom: Cr_2 (0), Cr_3 (2), Cr_4 (0), Cr_5 (0.93), Cr_6 (0.33), Cr_7 (0.29), Cr_8 (0), Cr_9 (0.22), Cr_{10} (0.2), Cr_{11} (0.55), Cr_{12} (1.67), Cr_{13} (1.06), Cr_{14} (0.74), and Cr_{15} (0.48).

for the predicted dimer-growth structures. Su and Armentrout measured the collision-induced dissociation of Cr_n^+ clusters and found a distinct even-odd alternation in dissociation energies for $n < 10$ [12]. More remarkably, they observed dimer loss for n up to 6. Both observations are consistent with the dimer-growth structures, even though the binding of the clusters may be altered by the positive charge. We recently measured photoelectron spectra of size-selected anion Cr clusters and found significant differences between the even and odd clusters for $n < 12$ [13]. The spectra of the even ones show distinct peaks and gaps near the Fermi level while the odd clusters all show more congested spectra near the Fermi level due to the electronic states of the odd atom [14]. The even-odd alternation in the electronic structure of the small Cr clusters is a natural consequence of the even-odd structure variations.

It is of particular interest to compare the magnetic properties of small Cr clusters with that of the bulk, which is antiferromagnetic [5,15]. Previous theoretical studies using bulk bcc structures for Cr_9 and Cr_{15} found them

TABLE I. Binding energies (BE) in eV of the Cr_n ($n = 2-15$) clusters of the dimer growth structures and other isomers for a few small clusters ($n = 3-5$).

n	Structure	BE	n	Structure	BE
2	$D_{\infty h}$	2.28	6	D_{3h}	10.72
3	C_{2v}	3.30	7	C_{2v}	13.46
	$D_{\infty h}$[a]	2.93	8	D_{4h}	16.57
	D_{3h}[b]	2.21	9	C_{2v}	18.82
4	D_{2h}	5.85	10	D_{4h}	21.66
	C_{2v}[c]	5.90	11	D_{4h}	24.78
	D_{4h}[d]	5.68	12	C_{2v}	29.39
	T_d[e]	4.24	13	D_{4h}	33.75
5	C_{2v}	8.48	14	C_{4v}	38.10
	D_{3h}[f]	8.19	15	D_{4h}	42.03
	C_{4v}[g]	6.97			
	D_{5h}[h]	6.87			

[a]Linear. [b]Equal lateral triangle. [c]Rhombus. [d]Square.
[e]Tetrahedral. [f]Trigonal bipyramid. [g]Square pyramid.
[h]Pentagonal ring.

to be antiferromagnetically coupled [16]. We discovered that the fully relaxed clusters are, in fact, all antiferromagnetically ordered with an anisotropic distribution of magnetic moments, depending on local atomic coordination. From Cr_3 to Cr_{11}, the local moments of the capping atoms are much higher than that of the dimer atoms due to the quasiatomic electronic states in the capping atoms and the strong intradimer $3d$-$3d$ interaction. Notice that for Cr_3 and Cr_{11}, the local moments on the dimer atoms are negligible due to the extremely short dimer bonds in these clusters (Fig. 2). An even-odd alternation of net moments for clusters up to Cr_{11} is again observed with small moments for the even and large moments for the odd (Fig. 2). On the other hand, for Cr_{12}–Cr_{15}, the local magnetic moments of the atoms on the cube corners are relatively high while those of the central atoms are very low due to the low coordination of the corner atoms and the high coordination of the central atoms, respectively. Interestingly, the Cr_{12}–Cr_{15} clusters all show antiferromagnetic ordering similar to that in the bulk, where the local atomic spins of the same atomic layer are parallel while those on neighboring atomic layers are antiparallel [17]. A similar magnetic structure is clearly observed in the Cr_{12}–Cr_{15} clusters. It is also noteworthy that our optimized Cr_{12} cluster appears extremely similar to a fragment of the Cr(100) surface [17]. We found that the photoelectron spectrum of Cr_{12} [13] is also strikingly similar to the Cr(100) surface photoemission spectrum [17,18], providing indirect evidence for the validity of the predicted cluster structures.

A previous experiment (for $n = 9-31$) showed no deflection for Cr_n clusters in an inhomogeneous magnetic field and concluded that these clusters can possess net moments no more than $0.77\mu_B$ per atom [19]. New generations of similar experiments are planned in which

the moments can be more sensitively detected to be able to verify the current predictions quantitatively [20]. Other experiments, such as chemisorption [21], may also be used to examine the structures of the clusters. The unique dimer growth structures should produce significant differences in the chemisorption behavior between the even and odd clusters.

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