Electronic structure and magnetism of small V and Cr clusters

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The electronic structure and magnetism of V_9, V_{15}, Cr_9, and Cr_{15} clusters having body centered cubic (bcc) geometry have been studied using a Gaussian orbital basis and the local spin density approximation. For V_9 and Cr_9, calculations were made for several different lattice spacings. Our calculated moment of $0.33\mu_B$ of V_9 is much smaller than the previously calculated $2.89\mu_B$ and is in very good agreement with a recent experiment. Our calculated moments of $0.67\mu_B$, $0.07\mu_B$, and $0.40\ \mu_B$, respectively for Cr_9, V_{15}, and Cr_{15} at the 0 K bulk lattice spacing are also in good agreement with experiment. But Cr_9 was found to have a transition near the bulk lattice spacing such that the moment becomes very large above the room temperature lattice spacing. Calculations of V_9 and Cr_9 at various interatomic distances show that they go through small magnetic moment to large moment transitions at certain distances, similar to the nonmagnetic to magnetic transition in bulk phase. The density of states profiles of V_{15} and Cr_{15} show the features characteristic of the bulk as had been the case in our previous calculations of Fe, Ni, and Cu.

I. INTRODUCTION

Small clusters of various sizes have been studied extensively in recent years in the hope of using them as a model for localized effect problems in solids and also for observing new properties which could not be obtained in solids.[1–13] Transition metal clusters are of special interest because transition metal elements play important roles in catalysis.[1]

In recent years, microclusters of various sizes have been made in laboratory and their properties were measured in great detail.[5–8] For alkali metals, the abundance characteristics experimentally observed could be explained very nicely with the shell model description of jellium clusters.[5] For transition metal clusters, it has been found experimentally as well as theoretically that most clusters have magnetic moments even though the elements do not have moments in their bulk phase.[8,11,12] On the basis of results of many cluster calculations it has been generally believed that cluster atoms have larger average magnetic moment per atom value than the atoms in the bulk phase.[9,11–13] Such a conclusion is reasonable because from many surface calculations, surface atoms are found to have a tendency to have larger magnetic moments than bulk atoms and clusters have large surface to volume ratio.

There has been some recent experimental measurement of magnetic moments using the Stern-Gerlach method.[7,8] The results indicated that clusters do not have as large magnetic moments as had been predicted by calculations.[12,13] The temperature and external magnetic field dependence was characteristic of paramagnetic materials. This problem was immediately resolved very nicely by Khanna and Linderoth using the superparamagnetic model of clusters.[14] Based upon such a superparamagnetic model, the cluster moments were estimated to be indeed larger than the bulk moment, in agreement with calculations.

Recently, Douglass, Bucher, and Bloomfield performed magnetic moment measurement of some small clusters and have found the upper limit of magnetic moments of $0.59\mu_B$ and $0.77\mu_B$ for V_9 and Cr_9 clusters, respectively.[8] These magnitudes are very small compared to the prediction of calculations, which are $2.78\mu_B$ and $3.89\mu_B$, respectively.[12,13] The geometry of the real cluster is not known and the difference between the geometry assumed in the calculation and the real cluster geometry could possibly be reasoned to be the origin of this discrepancy. Also, even if the geometry is the same, there are indications that the interatomic spacing in the cluster is not the same as that of the bulk. But, even assuming such uncertainties, the gap between the theoretical and experimental magnitudes seems too large considering the previous reasonable agreement between the calculated and experimental results.[6,9] Vanadium and chromium are interesting elements among $3d$ transition elements in the sense that they have paramagnetic and antiferromagnetic properties, respectively, in their bulk ground state although the atomic number difference is only one. Their atomic moments are very large in accordance with the Hund rule, but their magnetic moments are suppressed very much in the bulk phase. Only chromium has about $0.7\mu_B$/atom according to the information from neutron scattering experiments. Therefore it is interesting to find out what kind of magnetic behavior they will have in the cluster phase.

We have calculated the electronic and magnetic properties of V_9, Cr_9, V_{15}, and Cr_{15} clusters which have bcc geometry at 0 K lattice spacing in the bulk phase. To examine the change of cluster properties with atomic spacing, we also have made several other calculations of V_9, and Cr_9 clusters with varying atomic distance. Our calculated results for the magnetic moment are found to be in very good agreement with the recent experiment. But,

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for Cr_9 the cluster properties are very complex and a possibility of a very large magnetic moment seems to exist if the real cluster has bcc geometry. We also found that the density of states (DOS) of V_{15} and Cr_{15} clusters, which are obtained by Gaussian broadening of the cluster levels, exhibits the main characteristics of the bulk density of states very well as has been found to be the case in our previous calculations of Fe, Ni, and Cu clusters.[9,10]

II. METHOD

The method employed in this work has been described in detail before and only a brief description is given below.[9] We have used a Gaussian orbital as the basis for expanding the wave functions and adopted the local spin density functional approximation. The Gaussian basis used contained 14 s-, 9 p-, and 5d-type functions.[15] Including the angular dependence, this makes 66 independent functions per atom. To reduce the size of the Hamiltonian matrix in block diagonalized form, the basis was symmetrized in block diagonalized form according to the 10 irreducible representions of the full cubic O_h group. This is the only symmetry of the clusters considered in this work.

To avoid the difficulty of handling too many two electron integrals, which are encountered in typical Hartree-Fock calculations, charge densities were fit to an auxiliary basis set which was made of 14 s-type and 9 p-type Gaussian orbitals. A variational fitting method was used instead of the least squares fitting method. In the variational fitting, the quantities needed for fitting are just the same two electron integrals as those needed for evaluating the Coulomb matrix element. Furthermore, the Hartree part of total energy of the cluster is automatically evaluated if such a procedure is followed.

The exchange correlation potential used in this work is of the von Barth–Hedin type formula parametrized by Rajagopal, Singhal, and Kimball.[16] The corresponding matrix elements were calculated by direct numerical integration using a doubling grid developed for this purpose. Exploiting the generalized Unsold theorem, the grid needed for integration can be confined to the 1/48th zone for clusters with full cubic symmetry. The number of points used was about 1400 for the 9-atom clusters and about 2200 for the 15-atom clusters. This was tested and found to give very satisfactory results in overlap integral test calcuations.

III. RESULTS AND DISUSSION

A. V_9 and V_{15} clusters

V is a paramagnetic metal in bulk form even though the V atom itself is supposed to have a very large atomic moment according to Hund's rule. The properties of V clusters have been studied by Liu, Khanna, and Jena[12] using the discrete variational method (DVM).[3] They have studied the V_9 cluster extensively and predicted that V_9 has a very large moment of $2.89\mu_B$ but that the moment vanishes even for such a small cluster as a 15-atom cluster. They also found that the center atom magnetic moment of $1.38\mu_B$ goes to zero abruptly as the cluster lattice constant was contracted to below 0.9 times the bulk distance. V_{15} has also been considered by Salahub and Messmer[11] using the multiple scattering (MS) $X\alpha$ method.[2] The results agree with the DVM result in that the cluster is almost paramagnetic with virtually no spin splitting at all. The total magnetic moment per atom in either calculation is virtually zero.

Douglass, Bucher, and Bloomfield have recently measured the magnetic moments of clusters of nonferromagnetic materials using the Stern-Gerlach technique.[8] They measured moments for clusters of various sizes (8–99 atoms) and found that within the experimental uncertainty, V clusters do not have any magnetic moment. But, using the superparamagnetic relaxation model, the maximum magnetic moment per atom, consistent with their experiment, was estimated to be $0.59\mu_B$ for V_9, which is considerably smaller than the magnitude calculated by Liu, Khanna, and Jena. They also estimated that the magnetic moment per atom of V_{99} should be less than $0.18\mu_B$.

We have considered clusters with bcc geometry only in this work. The calculations were done with the lattice parameter of $a = 5.30$ a.u., which is the 0 K bulk lattice spacing. To examine the change of cluster properties as the lattice spacing changes, we have also calculated V_9 cluster properties with varying lattice constant, with up to 20% difference from the bulk value. The calculated results are summarized and compared with experimental and other theoretical results in Table I. As could be seen from the table, our calculated average magnetic moment per atom of $0.33\mu_B$ for V_9 and $0.07\mu_B$ for V_{15} clusters having bulk lattice spacing at 0 K are in very good agreement with the experiment.

The magnetic moment of $0.33\mu_B$ for V_9 is maintained for a wide range of lattice spacings, but a sudden transition occurs when the lattice spacing is increased to 6.85 a.u. Beyond this lattice spacing, the cluster atoms are expected to assume mostly atomic characters. Such a small moment to large moment transition looks similar to the nonmagnetic to magnetic transition studied by Moruzzi, Marcus, and Pattnaik in transition metals.[17] From a two atom per cell calculation, they found that antiferromagnetism is favored at the lattice spacing of $a = 6.40$ a.u. On the other hand, their one atom per cell calculation, which could reveal ferromagnetic order only, shows that low spin state begins at $a = 6.58$ a.u. The small moment to large moment transition occurs in the 6.28–6.85 a.u. range for the V_9 cluster in our calculation which is about the same range as the bulk transition. To determine which is the equilibrium lattice spacing if the cluster were to have bcc geometry, we have calculated the cluster total energies and the results are also shown in Table I. From the total energy information, it could be seen that its equilibrium lattice spacing should be somewhere in the 5.2–5.5 a.u range. This is smaller than the bulk spacing, which means a free V_9 cluster should be contracted with respect to the bulk V lattice spacing. We believe that

TABLE I. Magnetic moments and the total energy for V_9 and V_{15}: μ indicates the average magnetic moment/atom in μ_B units. μ_1, μ_2, μ_3, and μ_{int} indicate the local moments for center, first shell, second shell atoms, and the interstitial moments, respectively. Experimental data is from Ref. 8. Total energy/atom of the cluster is also shown (in Ry units).

	μ	μ_1	μ_2	μ_3	μ_{int}	E_{total}
V_9 (a=4.57)	0.33	-0.02	+0.17		+1.70	-1882.202
V_9 (a=5.14)	0.33	-0.06	+0.21		+1.32	-1882.219
V_9 (a=5.54)[a]	0.33	-0.12	+0.26		+1.03	-1882.218
V_9 (a=5.71)	0.33	-0.17	+0.28		+0.98	-1882.213
V_9 (a=6.28)	0.33	-0.67	+0.39		+0.53	-1882.175
V_9 (a=6.85)	2.78	-2.14	+2.69		+5.13	-1882.175
V_9[b]	2.89	-1.38	+3.42			
V_9 (Expt.)	< 0.59					
V_{15}(a=5.54)	0.07	+0.08	+0.04	+0.04	+0.35	
V_{15}[c]	0.07	+0.1	-0.0	+0.2		
V_{15}[b]	0.07	-0.02	+0.02	-0.03		

[a]0 K bulk lattice spacing.
[b]Reference 12.
[c]Reference 11.

the large moment observed by Liu, Khanna, and Jena is relevant to our large moment solution at the large lattice spacing. But the magnetic transition occurs at different lattice spacings in the two calculations, resulting in good agreement with the experiment in our calculation.

The investigation of local atomic properties in the cluster provides more detailed information. To estimate the local atomic moment on each atomic site in the cluster, we have used small nonoverlapping cubic regions surrounding each atoms as the domain belonging to each atom. Because such a shape is only an approximate form of the Wigner-Seitz cell, some portion of our interstitial contribution should belong to the local moment and our local moments are good only for qualitative purposes. The local moments calculated by this procedure for V_9 are also summarized in Table I. The magnetic moments at each atomic site when the cluster has 0 K bulk lattice spacing were $-0.12\mu_B$ and $+0.26\mu_B$, respectively, for center and surface atoms. These are substantially smaller numbers than the magnitudes reported by Liu, Khanna, and Jena[12] This could have been expected from the very small magnetic moment of $0.33\mu_B$ of ours compared to the large moment of $2.89\mu_B$ of their result. It could also be seen that these local moments grow larger gradually as the lattice spacing increases, until it comes to a transition point at about 20% larger lattice spacing than the bulk. Liu, Khanna, and Jena reported a sudden disappearance of the center atom moment as the lattice spacing is decreased to about 0.9 times the bulk spacing. The moment at the center site in our case increases very suddenly to a large magnitude as the lattice spacing is increased to about 1.2 times the bulk spacing.

The calculation of V_{15} cluster was done only at a = 5.54 a.u., which is the 0 K bulk lattice spacing. The calculated magnetic moments of V_{15} are also shown in Table I. In agreement with the two previous calculations[12,13] we find that the magnetic moment has already completely disappeared. The small moment of $0.07\mu_B$ is due to the odd number of electrons in the cluster (there are 173 spin up and 172 spin down electrons in the cluster). Such a feature could also be confirmed in the local moments which are $+0.08\mu_B$, $+0.04\mu_B$, and $+0.04$ μ_B, respectively, for the center, first, and second shell atoms. This indicates that V atoms do not possess any moment even for such a small size cluster as the 15 atom cluster.

B. Cr_9 and Cr_{15} clusters

Cr is known to have antiferromagnetic ordering in bulk form and it is an interesting question whether a small cluster such as Cr_{15} could show a tendency toward antiferromagnetic ordering. Cr clusters have been studied theoretically by several groups previously.[11,13] Salahub and Messmer have used the MS $X\alpha$ method[2] and found the average magnetic moment or atom of $0.80\mu_B$ for a Cr_{15} cluster.[11] They also observed large magnetic moments on each atomic site which has an alternating sign of polarization from shell to shell. The magnetic moment they found was $-0.7\mu_B$, $+4.1\mu_B$, and $-3.4\mu_B$ for the center, first, and second shell atoms, respectively. The magnitudes of local moment seems to be too large compared to the bulk atomic moments of $0.7\mu_B$, but it is interesting to see that they are already showing symptoms of antiferromagnetic ordering in such a small size. Pastor, Dorantes-Davila, and Benneman used a model Hamiltonian with some adopted parameters to study wide variety of Cr clusters in size and geometry.[13] For bcc structured clusters, they reported a large magnetic moment per atom of $3.89\mu_B$ for Cr_9 which becomes a relatively small $0.33\mu_B$ in Cr_{15}. They have also observed the antiferromagnetic ordering pattern from shell to shell in agreement with the previously reported result. The magnetic moment per atom at each atomic site of the cluster was found to be $-1.76\mu_B$, $+2.90\mu_B$, and $-2.74\mu_B$, respectively, for the center, first, and second shell atoms, which are also very large compared to bulk atomic mo-

ment. These magnitudes of local moments were reported to be very sensitive to the lattice spacing of the cluster. (For 2% difference in lattice spacing, the local moments varied by as much as about 10%)

Douglass, Bucher, and Bloomfield have measured the magnetic moments of Cr clusters[8] and analyzed their experimental data using the superparamagnetic model. They have found that the average magnetic moments of Cr_9 and Cr_{15} clusters should be less than $0.77\mu_B$ and $0.60\mu_B$, respectively. Obviously, the calculated magnetic moment of Cr_9 is too large compared to the measured values, although the results are compatible for Cr_{15}.

We have made calculations of Cr_9 and Cr_{15} clusters with bcc geometry, having 0 K bulk lattice spacing of $a = 5.30$ a.u. For Cr_9 cluster, calculations were done for several other lattice parameters to study the change of cluster properties depending on the lattice parameter. Our calculated results are summarized and compared with other calculated and experimental results in Table II. We have found that at the 0 K bulk lattice spacing the magnetic moment per atom is $0.67\mu_B$ for Cr_9 and $0.40\mu_B$ for Cr_{15}, which are in very good agreement with the measured upper limits of $0.77\mu_B$ and $0.60\mu_B$, respectively.[8] Our calculated magnetic moment of Cr_9 is much smaller than that found by Pastor, Dorantes-Davila, and Benneman using their model Hamiltonian.[13] It is also clear that the average magnetic moment of cluster decreases as the cluster size grows, but does not converge to the bulk properties as fast as V clusters did.

Although the calculated moment of Cr_9 was very satisfactory for 0 K bulk spacing, we immediately discovered that there exists a transition to a large moment state near the bulk lattice spacing. As soon as the lattice spacing was changed to the room temperature value of $a = 5.45$ a.u., we have found that the moment of Cr_9 suddenly jumps to $3.78\mu_B$. This is the same kind of transition we observed in V_9 cluster, but in this case the transition occurred near the bulk lattice spacing. To examine the properties more closely, we have done several more calculations with varying lattice parameter and have found that the total energy of Cr_9 cluster behaves in a very complex way. The cluster total energies are tabulated in Table II. The total energy drops suddenly around the bulk lattice spacing and then increases almost linearly at larger lattice parameters. Such a drop in energy is accompanied by a drastic change of the cluster magnetic moment from $0.67\mu_B$ to $3.78\mu_B$ also.

In a two atom per cell calculation, Moruzzi, Marcus, and Pattnaik also have found that Cr begins to have antiferromagnetic ordering if the lattice constant is increased by only 2% from the experimental spacing of $a = 5.44$ a.u.[17] Their finding of a nonmagnetic to antiferromagnetic transition near the bulk lattice parameter looks very similar to what we observe in our cluster, although we cannot say definitely that we observe antiferromagnetism in Cr_9.

Another interesting aspect of the total energy is that it has another minimum at a shorter lattice spacing of around 4.3 a.u. This metastable state has a small moment of $0.67\mu_B$ in agreement with the experiment. As the lattice spacing is made even shorter, the cluster moment vanishes, but this time accompanied by a smooth total energy variation. It is not possible to say at the moment what kind of geometry the real Cr_9 cluster has and what its lattice parameter is, but if it has bcc symmetry, two different moments of $0.67\mu_B$ and $3.78\mu_B$ are possible for the Cr_9 cluster.

The local atomic moment at each cluster site was also determined in the same way as has been described previously. Our calculated local moments for the center and surface atoms for Cr_9 were $-0.54\mu_B$ and $+0.71\mu_B$, respectively, which are very small in magnitude compared

TABLE II. Magnetic moments and the total energy for Cr_9 and Cr_{15}: μ indicates the average magnetic moment/atom in μ_B units. μ_1, μ_2, μ_3, and μ_{int} indicate the local moments for center, first shell, second shell atoms, and the interstitial moments respectively. Experimental data are from Ref. 8. Total energy/atom of the cluster is also shown (in Ry units).

	μ	μ_1	μ_2	μ_3	μ_{int}	E_{total}
Cr_9 (a=3.82)	0.00	0.00	0.00		0.00	-2082.556
Cr_9 (a=4.10)	0.00	0.00	0.00		0.00	-2082.598
Cr_9 (a=4.36)	0.67	-0.12	+0.45		+2.42	-2082.779
Cr_9 (a=4.63)	0.67	-0.15	+0.43		+2.52	-2082.724
Cr_9 (a=4.90)	0.67	-0.26	+0.56		+1.66	-2082.666
Cr_9 (a=5.30)[a]	0.67	-0.54	+0.71		+0.69	-2082.651
Cr_9 (a=5.45)	3.78	-1.45	+3.16		+9.45	-2083.011
Cr_9 (a=6.00)	3.78	-2.31	+3.52		+7.40	-2082.934
Cr_9[b]	3.89	-2.71	+4.71			
Cr_9 (Expt.)	< 0.77					
Cr_{15} (a=5.30)	0.40	-0.12	+0.16	+0.36	+2.61	
Cr_{15}[c]	0.80	-0.7	+4.1	-3.4		
Cr_{15}[b]	0.33	-1.76	+2.90	-2.74		
Cr_{15}(Expt.)	< 0.60					

[a]0 K bulk lattice spacing.
[b]Reference 13
[c]Reference 11.

to the large moments of $-2.71\mu_B$ and $+4.71\mu_B$ found by Pastor, Dorantes-Davila, and Benneman.[13]

For Cr_{15}, calculations were made only at the 0 K bulk lattice spacing of $a = 5.30$ a.u. The results of our calculation as well as other available data on Cr_{15} are summarized in Table II. Our calculated magnetic moment of $0.40\mu_B$ is comparable to the previously reported moments, although the magnetic moments are slightly different in all three calculations. For this case, all three calculated moments are comparable to the experimental result, which sets the maximum moment to be $0.60\mu_B$.[8] But it turns out that the differences between our results from the previous works are more profound than it appears. The major difference between our result and the previous results was encountered in the magnitude of the local moments of the atoms and the absence of antiferromagnetic ordering symptoms in our result. As could be seen from the table, our magnetic moments on each shell site are $-0.12\mu_B$, $+0.16\mu_B$, and $+0.36\mu_B$ for the center, first, and second shell atoms, respectively, and are about an order of magnitude smaller than the values reported before.[11,13]

An even more significant difference may be that our magnetic moments do not show any sign of antiferromagnetic ordering at all. We believe the negative polarization of the center site atom is due to the minority spin domination behavior which is commonly observed in typical transition metal clusters.[9,12,13] In clusters, because of large surface polarization, minority spin electrons have a tendency to escape to the center site. Therefore, a $-0.54\mu_B$ and $+0.71\mu_B$ combination of magnetic moments in Cr_9 is probably the result of this and should not be viewed as a sign of antiferromagnetic ordering. The tendency of the minority spin domination at the center site still exists for Cr_{15}, as could be seen from the $-0.12\mu_B$, $+0.16\mu_B$, and $+0.36\mu_B$ combination, but the magnitude of center atom moment is considerably reduced. It may be concluded therefore that the local atomic properties converge very slowly to the bulk values as the cluster size grows.

C. DOS similarity

How fast do the properties of the center atom converge to a typical bulk atomic property as the cluster size becomes large? Is it good enough to include up to second nearest neighbors as the surrounding atoms to simulate bulk environment for an atom? This latter question is interesting in itself and it has to be answered before free clusters can be used as a model for impurity problems in a solid. The result of the previous analysis of local moments of cluster atoms is not enough to answer such questions.

To better understand the local atomic properties in the cluster, we have done an analysis similar to our previous work in which we plot the density of states of the cluster by broadening each cluster levels by a Gaussian.[9] In this scheme, the DOS per atom is given by the relation

$$G(E) = \frac{1}{N\sqrt{2\pi}\sigma} \sum g_i \exp \frac{-(E - E_i)^2}{2\sigma^2} \qquad (1)$$

in which N is the number of cluster atoms, g_i is the degeneracy of level E_i, and σ is the width parameter. The broadening width parameter was chosen to be 0.2 eV, which is the same as the one used before for Fe and Ni clusters, although it is expected that the d-type wave functions in V and Cr clusters are more delocalized compared to Fe or Ni. The results for V_{15} and Cr_{15} are shown in Figs. 1 and 2, respectively, where the total cluster DOS and the rough sketch of the bulk DOS (Ref. 18) are overlapped for direct comparison. In these figures, the thick curve is for the cluster DOS and the thin curve is for the bulk DOS. It is obvious from the figures that the cluster DOS simulates bulk DOS very nicely in both clusters below the Fermi level, which is the $E = 0$ position in the graph. For example, the main three-peak structure in the bulk is also found in the cluster, and the small two-peak structure just below the Fermi level is also manifested in the cluster DOS.

The two curves have minima at around -3 eV in common and the broad peak feature just below that is also well matched. Above the Fermi level, V_{15} cluster levels generate the next peak too early so that its peak occurs at that of a minimum in the bulk DOS. But, for the Cr case, due to the narrowing of the bulk bandwidth, the peak positions are shifted only just a little bit from each other. We cannot hope that clusters as small as a 15-atom cluster made up of transition element atoms with relatively delocalized d electrons exhibit the very delocalized behavior of the bulk state very nicely. But it is clear that the cluster levels simulate the bulk DOS characteristics reasonably well and simulate better toward the right-hand side of the Periodic Table because the elements have more localized d electron character toward the right-hand side of the Periodic Table. In fact, our previous studies have already shown that there exists remarkable similarity between the cluster and bulk DOS in Fe, Ni, and Cu.[9] But, such similarity should not be understood as indicating that the local atomic properties, especially those of the central atom, are also similar to bulk atomic properties.

To study the local properties, we have plotted the local DOS by integrating the quantity

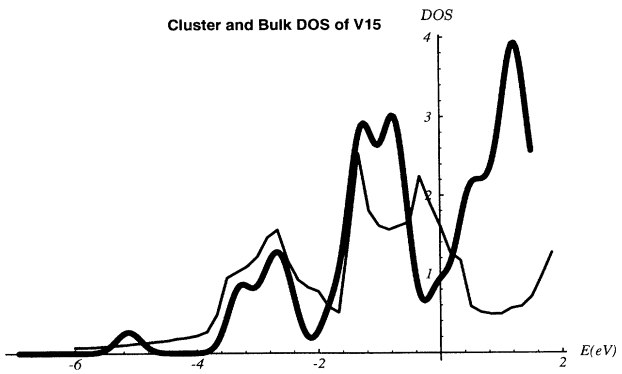

FIG. 1. Total DOS (in arbitrary units) of V_{15} and the bulk DOS. The thick curve is for the cluster DOS and the thin curve is for the rough sketch of bulk DOS.

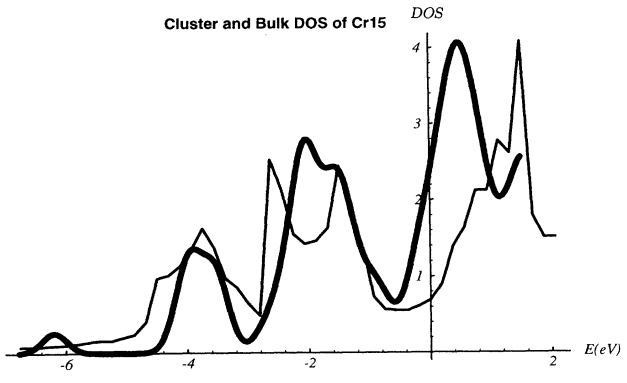

FIG. 2. Total DOS (in arbitrary units) of Cr_{15} and the bulk DOS. The thick curve is for the cluster DOS and the thin curve is for the rough sketch of bulk DOS.

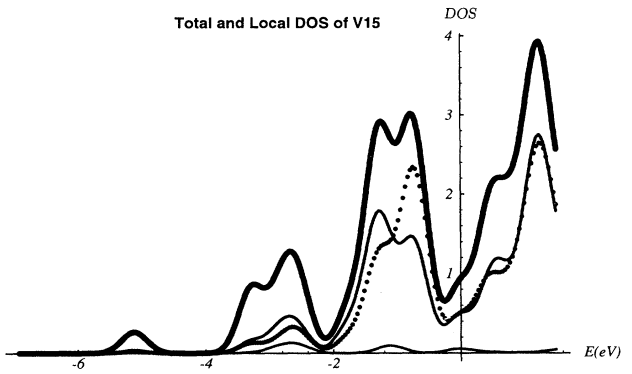

FIG. 3. Total DOS and the local DOS of V_{15} (in arbitrary units). The thickest curve is for the total DOS and the thick and dotted curves are for the first and second shell local DOS. The center atom local DOS is shown as the curve at the bottom region.

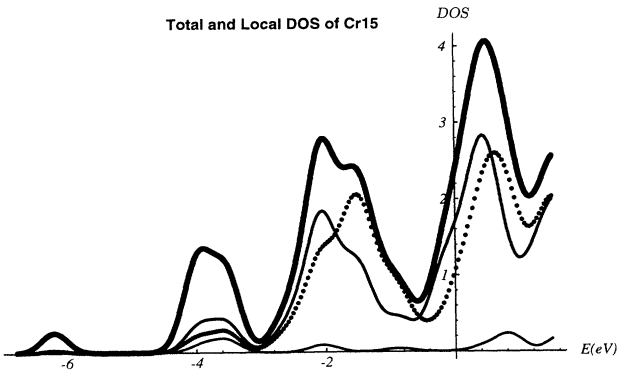

FIG. 4. Total DOS and the local DOS of Cr_{15} (in arbitrary units). The thickest curve is for the total DOS and the thick and dotted curves are for first and second shell local DOS. The center atom local DOS is shown as the curve at the bottom region.

$$n(E,\mathbf{r}) = n(E)|\psi_E(\mathbf{r})|^2 \quad (2)$$

around each atomic site, where $n(E)$ is total DOS at energy E.[4] The domain of integration used is the same nonoverlapping cubical region as has been used to determine the local magnetic moment.

The results of such analysis are shown in Figs. 3 and 4 for V_{15} and Cr_{15} clusters, respectively. In the figures, thick curves indicate the total DOS and the thin and dotted curves are for the first and second shell atoms, respectively. The thin curve at the bottom region indicates the center atom local DOS. From the figures, it is clear that the similarity in the total DOS is the artifact of combined contribution from the local DOS of each cluster site. For example, the double peak feature of bulk DOS just below the Fermi level is simulated by the two independent peaks which belong to the first and second shell atoms.

We have seen that the DOS similarity between the cluster and bulk is mainly due to the combined contribution of shell atoms. But how close does the center atom DOS resemble bulk DOS? As the weak curve at the bottom region shows, it is very clear that there is very little similarity at all. We believe that this is a clear indication that the center atom cannot be assumed to be in reasonable approximations at the bulk environment for such small clusters. This means that a very large cluster or proper embedding method is needed to handle impurity problems in a solid using a cluster model.

IV. SUMMARY

We have calculated the electronic and magnetic properties of V_9, V_{15}, Cr_9, and Cr_{15} clusters. For V_9 and Cr_9, calculations were done for several lattice spacings. Magnetic moments of all the calculated clusters with bcc geometry were found to be in good agreement with a recent experiment, except for Cr_9 which shows complex behavior of the total energy. If a real cluster of Cr_9 has bcc geometry, our result suggests that it should exist in a large moment state, but a small moment metastable state might also exist.

The cluster density of states obtained by Gaussian broadening of the levels is found to simulate the bulk density of states very well, exhibiting all the main characteristics and comparable bandwidth. But, our local density of states analysis indicates that the center atom in the cluster which has up to second shells of neighbor atoms has very little similarity to the bulk. This implies that a free cluster model is not suitable for localized effect problems in solids such as impurity problems, if it is not accompanied by a very careful embedding scheme.

Note added in proof. We have recently found that there exists a high-spin state as well as a low-spin state for some clusters in certain lattice spacing ranges, as has been the case for many transition-metal solids. Using a large-moment potential as the input, we have found that in addition to the low-spin state reported in the paper, a

high-spin state also exists for both the V and Cr clusters for some range of lattice parameters. These high-spin states have large moments which are comparable to the large moments reported by other authors using different methods. A more detailed account of this note will be reported later.

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