Possible magnetism in small palladium clusters

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Possible magnetism of small palladium clusters having cubic geometry has been studied using the Gaussian orbital basis and the local spin-density approximation. Extensive calculations have been done on Pd_{19} clusters with face-centered-cubic symmetry by varying atomic spacing parameters. Possible magnetism of the Pd_{15} cluster with body-centered-cubic symmetry has also been studied. Fixed moment calculations were done to find all possible metastable states of the cluster. In addition to a nonmagnetic state, the Pd_{19} cluster is found to have a magnetic state with a moment of $0.32\mu_B$. The two states are very close in total energy but the magnetic state has slightly lower total energy. The Pd_{15} cluster is found to have only one magnetic state with a moment of $0.53\mu_B$. From our calculations, we conclude that palladium clusters are very likely to be magnetic although the magnetic moment is very small. [S0163-1829(98)00229-X]

Small clusters are very interesting objects because they could be used as a model for localized effect problems in solids and also because they are expected to show properties which are different from atoms or solids.[1,2]

It is generally accepted now that $3d$ transition-metal clusters are usually magnetic with larger magnetic moments per atom than in solid phase.[3,4] It has also been found that even vanadium and chromium clusters are possibly magnetic if their size is small enough.[5–7] This is interesting because vanadium is nonmagnetic in solid phase. But on the other hand, vanadium atom is magnetic according to Hund's rule. Since a cluster is an object which lies between an atom and bulk, it is natural to imagine that small vanadium clusters could be magnetic.

Out of $4d$ elements, ruthenium, rhodium, and palladium are isoelectronic to iron, cobalt, and nickel, respectively, which are their $3d$ partners. But none of these $4d$ metals are magnetic in bulk phase. Therefore, possible magnetism of such 4d element clusters has been a very interesting subject.[8–13] In fact, very large magnetic moments of $4d$ clusters have been predicted by calculation and it was confirmed that the rhodium clusters indeed have large moments immediately afterwards from the experiment.[11,12] But the observed rhodium cluster moments were not as large as the predicted moments. Although Rh clusters were magnetic, Cox *et al.* could not confirm magnetism of Ru and Pd clusters from their experiment.[12] But assuming superparamagneic behavior of clusters, Cox *et al.* did not rule out the possibility of magnetism of these clusters. They set the upper limit of $0.40\mu_B$ per atom for the Pd_{13} cluster and $0.13\mu_B$ per atom for the Pd_{105} cluster from their experiment. Zhang *et al.* performed discrete variational method calculations of octahedral 6-atom $4d$ clusters, intending to obtain binding energy trend of small $4d$ clusters. They found Ru and Rh clusters are magnetic but the Pd cluster is not.[10] Piveteau *et al.* have studied on the magnetic properties 13-atom $4d$ clusters. They found a small magnetic moment in the icosahedral geometry but zero moment in the face-centered-cubic cluster. It has also been reported from the local-density calculation that Pd chains or islands on the surface of Ag are not magnetic although Ru and Rh islands are magnetic.[14] It is therefore still controversial whether small Pd clusters are magnetic or not.

We have performed linear combination of Gaussian orbital method calculations to study the possible magnetism of small palladium clusters with face-centered (fcc) and body-centered (bcc) structures. The method employed in this work has been described in detail before and only a brief description is given below.[4] We have used Gaussian orbitals as the bases for expanding wave functions and adopted the local spin-density approximation. The Gaussian bases used contained 17 s-, 11 p-, and 8 d-type functions.[15] Including angular dependences, They make 90 independent basis functions per atom. To reduce the size of the Hamiltonian matrix in block-diagonalized form, the bases were symmetrized in block-diagonalized form according to the ten irreducible representions of the full cubic O_h group. Also, to avoid the difficulty of handling too many two electron integrals which are encountered in typical Hartree-Fock-type calculations, charge densities were fit to an auxiliary basis set which was made of 17 s-type and 11 p-type Gaussian orbitals. A variational fitting method which minimizes the total-energy difference due to fitting was used instead of the least-squares fitting method which minimizes charge-density difference.[16] The exchange correlation potential used in this work is of the von Barth–Hedin-type formula parametrized by Rajagopal, Singhal, and Kimball.[17] The corresponding matrix elements were calculated by direct numerical integration using a doubling grid developed for this purpose.[4] Exploiting the generalized Unsold theorem, the grid needed for a numerical integration can be confined to the 1/48th zone for clusters with full cubic symmetry.

Moruzzi *et al.* have introduced the idea of fixed moment calculation to determine all possible metastable states of bulk $3d$ transition-metal systems.[18] In this procedure the system is forced to have a fixed magnetic moment, defying the ordinary Fermi occupation rule. If such calculations are performed for several different fixed moments, a total-energy curve is obtained from which all possible metastable states could be determined.

It has been reported that clusters can also have many different magnetic moments with very small differences in total energy.[7] This indicates a possibility that clusters in real ex-

periments are composed of clusters with several magnetic moments. Therefore, experimentally observed moments may be just the thermal averages of several possible moments. In order to find all possible metastable states in a cluster, we performed fixed moment calculations for the cluster. After fixed moment states were obtained, we then allowed the system to relax so that the cluster converges to one of its metastable state. Such a procedure is equivalent to obtaining self-consistent results from many different initial potentials. By such procedure, it is hoped that all possible magnetic states of a cluster could be found. Of course, all but one of the states will be metastable which corresponds to local minima of the total-energy configuration. We believe such metastable states correspond to states with different total spin of the cluster which cannot be determined from calculations using the present density-functional theory.

To investigate possible magnetism of palladium clusters, we have studied the 19-atom cluster with fcc geometry and the 15-atom cluster with bcc geometry. Palladium has fcc symmetry in bulk phase. Our Pd_{19} atom cluster has the geometry of one atom surrounded by 12 nearest neighbors and six next-nearest neighbors and the Pd_{15} cluster has one atom surrounded by eight nearest neighbors and six next-nearest neighbors. Our calculation was restricted to clusters with full cubic symmetry although no information is known about the real cluster structure. However, to investigate the effect of lattice constant on the magnetic property, we have done calculations with several different atomic spacings for the 19-atom cluster. To find all possible metastable states of a cluster, states with several different fixed moments including very small and very large moments were determined as the first step. Each fixed moment state was then relaxed so that it converges to a self-consistent state.

We started our calculation of the Pd_{19} cluster with the lattice constant of 7.35 a.u. which is the experimental lattice constant in bulk phase at room temperature. We found there are two possible states for this cluster. One state did not have any magnetic moment but the other state was magnetic with a moment of $0.32\mu_B$ per atom. The magnetic state was found to have a slightly less total energy, although the energy difference between the two states was very small.

If the lattice constant is reduced in bulk phase, magnetic moment is usually quenched because of band broadening. Such a trend is also expected in cluster systems. We performed calculations with reduced lattice spacings to determine whether the state with the magnetic moment disappears if the lattice spacing is sufficiently reduced. We reduced the lattice constant down to 6.68 a.u which is about 9% smaller than the bulk lattice constant. We found that even at such reduced lattice spacing, the state with magnetic moment did not disappear.

We also performed calculations with increased lattice spacings. If distances between atoms are far enough, it is expected that a cluster will have only magnetic states, because of band narrowing. From the energy band calculations, it has been reported that a sudden transition from a nonmagnetic to a ferromagnetic state with a moment of $0.31\mu_B$ occurs when the lattice constant is about 7.735 a.u.[19] This corresponds to a 5.5% increase from the equilibrium lattice constant. We found that at about 7.68 a.u. which is about 4% larger than the bulk lattice constant, the nonmagnetic state

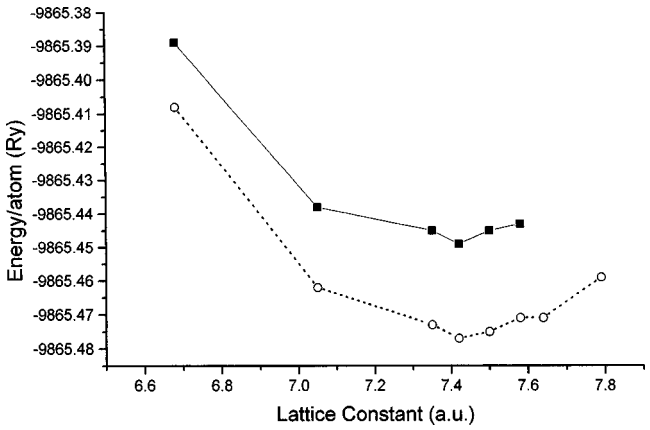

FIG. 1. Total energy per atom of the 19-atom palladium clusters. The solid squares indicate nonmagnetic states and the open circles indicate magnetic states.

disappears and the cluster has only the magnetic state. Figure 1 shows the trend of total energy per atom when the lattice constants of the cluster are varied. In the figure, filled squares indicate energies of nonmagnetic states and open circles indicate energies of magnetic states. It can be seen that in all lattice spacings, magnetic states have lower total energies indicating they are the ground states. In Fig. 2, the total energy of the cluster depending on its magnetic moments is shown, when the lattice constant is 7.35 a.u. The data points include not only the fixed moment results but also the metastable states obtained from them. It is again clear from the figure that the state with $0.32\mu_B$ has the lowest energy indicating that the magnetic cluster is the ground state.

In our calculation, minimum of the cluster total energy was obtained at 7.42 a.u., whether the cluster is magnetic or nonmagnetic. Moruzzi *et al.* have also found that equilibrium lattice constant is around 7.42 a.u. from their local spin-density calculations of bulk palladium.[22] This is slightly larger than the experimental value of 7.35 a.u. It is interesting to note that palladium has its minimum calculated total energy at the same lattice constant whether it is in cluster or bulk phase. From our calculations, even with 9% reduced lattice spacing, the Pd_{19} cluster continues to have the magnetic as well as the nonmagnetic state.

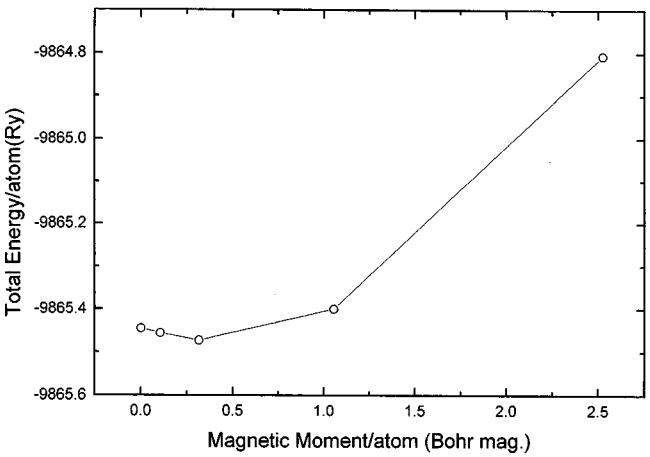

FIG. 2. Total energy per atom of the Pd_{19} cluster with lattice constant of 7.35 a.u.

TABLE I. Magnetic properties of palladium clusters: A denotes the lattice constant used for each cluster. μ indicates the average magnetic moment/atom in μ_B units. μ_0, μ_1, μ_2, and μ_{int} indicate the local moment of center, first shell, second shell, and interstitial site, respectively. $d\rho_0$, $d\rho_1$, and $d\rho_2$ indicates contact spin densities of the center, first-shell, and second-shell atoms, respectively. Total energy/atom of the clusters are also shown in Ry units. Pd_{13} data is from Ref. 13. Experimental data are from Ref. 12.

	μ	μ_0	μ_1	μ_2	μ_{int}	$d\rho_0$	$d\rho_1$	$d\rho_2$	E_{total}
Pd_{13} (fcc)	$A=7.42$ a.u.								
	0.00	0.00	0.00		0.00	0.00	0.00		−9365.90
	0.46	−0.03	0.39		1.26	−0.06	0.70		−9865.97
Pd_{15} (bcc)	$A=5.83$ a.u.								
	0.53	0.60	0.51	0.50	0.12	−0.21	−0.22	−0.24	−9865.38
Pd_{19} (fcc)	$A=6.68$ a.u.								
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−9865.39
	0.32	0.44	0.25	0.37	0.17	−0.17	−0.06	−0.27	−9865.41
	$A=7.42$ a.u.								
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−9865.45
	0.32	0.43	0.26	0.38	−0.03	−0.16	−0.09	−0.31	−9865.48
	$A=7.64$ a.u.								
	0.32	0.42	0.26	0.39	−0.07	−0.16	−0.09	−0.32	−9865.47
Experiment	<0.40								

To confirm the possibility of magnetism in palladium clusters, we have also done calculations of the Pd_{15} cluster with bcc geometry. For this cluster, the calculation was done for only one lattice constant of 5.83 a.u. The lattice constant was chosen such that the volume per unit atom is the same with that of the fcc bulk palladium. Unlike the 19-atom cluster, we found that the Pd_{15} cluster has only one state which is magnetic. The calculated moment was $0.53\mu_B$ per atom. The fact that palladium cluster is magnetic in bcc as well as fcc geometry seems to support the possibility that small palladium clusters are indeed magnetic.

We have summarized our calculated results of the fcc cluster with several lattice constants and the result of the bcc cluster with the lattice constant of 5.83 a.u. in Table I. For convenience, the previously reported result of the Pd_{13} cluster is also included in the table.[13] The Pd_{13} cluster was reported to have two states with magnetic moments of 0.0 and $0.46\mu_B$ as is given in the table. In the table, local magnetic moments and contact spin densities are also listed. Contact spin density is the spin density at the nucleus sites and is related to the magnitude of hyperfine splitting. As could be seen from the table, contact spin densities of the 15- and 19-atom clusters are all negative. The fact that contact spin densities are negative is an indication that the minority-spin electrons are dominant at the nucleus sites. This is a well-known feature in bulk phases. Such a thing happens because minority-spin electrons have tendency to move away from the majority-spin-dominated region when the system is magnetic. In bulk, minority-spin electrons either move to interstitial region or to the nucleus sites. But because surface atoms in a cluster do not provide interstitial region as in the bulk, the nucleus site regions seem to be the only places where the minority-spin electrons could dominate.

We have considered clusters with full cubic symmetry only in this work. But it should be mentioned that icosahedral geometry is frequently found to be more stable than the fcc clusters for the 13-atom clusters. As was mentioned earlier, the Pd_{13} cluster was found to be more stable in magnetic icosahedral structure than in nonmagnetic fcc structure.[9]

The Jahn-Teller effect is also known to be important in clusters. If a system geometry is distorted, its degenerate levels are furthur split into separate levels. Such a process usually raises the system energy, but in some cases the system energy is lowered by such a process.[20] Such Jahn-Teller distortion has been found to lower the energy in some very small clusters. But as the cluster size grows, clusters are expected to have geometries of high symmetry. We believe 15- and 19-atom clusters have a good chance of having high-symmetry structures.

Density of states (DOS) similarity between a bulk and cluster system is also an interesting subject. In our previous calculations, we have noticed a remarkable similarity between the bulk and cluster DOS in $3d$ metals.[4,7] Such a similarity has been observed experimentally for some $3d$ clusters recently.[21] We have done a similar analysis of the cluster DOS by broadening the cluster levels using Gaussians. In this analysis, each cluster level is replaced by a Gaussian of certain width. The bandwidth of a bulk palladium band is about 5 eV.[22] We found that the Pd_{19} cluster energy levels have almost the same bandwidth. But we found little similarity between the bulk and cluster DOS for palladium clusters. It is not clear why there is little DOS similarity between bulk and cluster phase palladium whereas there exists a remarkable similarity in $3d$ clusters. One possible reason could be that the valence electrons in $4d$ elements are less localized compared to valence electrons in $3d$ elements.

In conclusion, we have performed linear combination of Gaussian orbital basis calculations to study possible magnetism of palladium clusters. We find that the Pd_{19} cluster has a magnetic state as well as a nonmagnetic state for a wide

range of atomic spacings. The magnetic state has a magnetic moment per atom of $0.32\mu_B$. The Pd_{15} cluster has only one magnetic state with a magnetic moment per atom of $0.53\mu_B$. Our results indicate that there is a strong possibility that the palladium clusters are magnetic although the moment may be small. The DOS similarity between the cluster and bulk was also investigated but we found little DOS similarity for palladium clusters.

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