Abstract

In this communication, we report the equilibrium geometry, electronic and magnetic characteristics of MPd$_{12}$ clusters, obtained by using the density functional theory formalism, under spin-polarized generalized gradient approximation method. Unlike, bulk Pd metal, the Pd$_{13}$ cluster in its lowest energy structure, shows a magnetic moment of 8 $\mu$B with close packed icosahedral geometry. The substitution of one Pd atom with different 3d elements, leads to similar atomic configuration, with 3d transition metal element occupying the central position in the icosahedral structure. However, the magnetic characteristics of these clusters are significantly affected by the electronic configuration of the substituent element. The substitution of one Pd atom with Ti, V, Cr, Cu and Zn atom, reduces the total magnetic moment due to antiferromagnetic coupling between the moments of Pd atoms and 3d transition metal atom. For CrPd$_{12}$, the calculated value of the magnetic moment of 2$\mu$B, is the lowest. Unlike this, the substitution of Pd atom by Mn, Fe and Co enhances the magnetic moment of the cluster due to the ferromagnetic coupling of all the moments, the effect being most pronounced for Mn substitution as the MnPd$_{12}$ cluster carries a magnetic moment of 11$\mu$B. Substitution of Ni, which is isoelectronic with Pd, does not affect the magnetic moment of the cluster.

Introduction

During the last decade, a large number of investigations have been carried out for doped clusters [1] with a view to understanding their atomic and electronic structure. Based on these studies it is found, that the impurity atom can influence the geometry, electronic and bonding properties of the host clusters. One of the important questions in the study of transition metal clusters, is the estimation of the size of the cluster, when it shows the cooperative phenomenon as shown by the corresponding bulk materials like appearance of magnetism. In this connection, we have investigated the atomic and electronic structure of Pd$_{13}$ and Pd$_{12}$M (where M is the 3d transition metal element) clusters, with a view to understanding the
location of the transition metal atom in these clusters and its influence on the magnetic characteristics of these clusters. Although bulk Pd metal is diamagnetic in nature, its clusters of finite size are found to show significant magnetic moment. The choice of Pd$_{13}$ as the host cluster has been driven by its high stability and icosahedral symmetry.

**Computational Details**

The total energy calculation and geometry optimization of clusters were performed, using the density functional theory with Projector Augmented Wave (PAW) pseudopotential and plane wave basis set. The spin-polarized Generalized Gradient Approximation (GGA) [2] has been used to calculate the exchange-correlation energy. In order to check the reliability of the pseudo-potential used in the present work, test calculations were performed for bulk Pd. The cohesive energy and lattice constant thus calculated is found to be 3.718 eV/atom and 3.96 Å, which is in good agreement with the experimental values of 3.89 eV/atom and 3.89 Å, respectively.

**Results And Discussion**

Fig. 1(a) shows the ground state geometry of the Pd$_{13}$ cluster, which favors slightly distorted icosahedron structure. The Pd-Pd distance between the center and apex atom is found to be 2.59 Å. The separation between other Pd atoms varies between 2.71 Å to 2.79 Å. Most importantly, the Pd$_{13}$ cluster shows a total magnetic moment of 8µ$_{B}$. This is interesting as the bulk Pd metal is non-magnetic. The distortion in the symmetry of Pd$_{13}$ icosahedron is attributed to the John-Teller effect, which in turn causes the spin polarization in the Pd$_{13}$ icosahedron. The average binding energy of Pd$_{13}$ cluster is estimated to be 2.31 eV/atom. The removal of one atom from Pd$_{13}$ cluster and optimization of its structure, resulted in a similar skeleton for Pd$_{12}$ cluster with the same value of magnetic moment of 8µ$_{B}$ implying an increase in the local magnetic moment of each Pd atom. The structure of Pd$_{12}$ cluster is shown in Fig. 1 (b), which is almost similar to that of Pd$_{13}$ less the central atom.

The search for ground state geometry of MPd$_{12}$ clusters has been derived from the icosahedron configuration obtained for Pd$_{12}$. The interaction of an impurity atom with such a homo-atomic cluster can lead to three different possibilities viz., (a) the impurity atom can occupy the center of the cage formed by the host cluster (endo-hedral), (b) the impurity atom can replace one atom from the network of the host cluster (substitutional) and (c) the impurity atom can adsorb on the surface of the host cluster (exo-hedral). In all cases we found, that for the lowest energy structure, the 3d transition atom...
is occupying the central position in the icosahedron. However, there are interesting differences in the magnetic behavior of these clusters, depending on the location of the M atom. For example, in case of CrPd\textsubscript{12} cluster we find that all three isomers, which differ in their energy, have also got different magnetic moments.

In fig. 2, we have plotted the variation in the magnetic moment of MPd\textsubscript{12} clusters with different transition metal atoms and compared them with the M-Pd dimers. From this figure it can be seen that both M-Pd dimer and MPd\textsubscript{12} cluster show maximum magnetic moment. For M-Pd, the magnetic moment increases linearly up to Mn and then decreases in the same way. However, in case of MPd\textsubscript{12} clusters the magnetic moment shows a decrease up to Cr and then there is a sharp increase for MPd\textsubscript{12} after which the magnetic moment decreases linearly. While M-Pd clusters show lowest magnetic moment for Zn-Pd, the MPd\textsubscript{12} shows a minimum at CrPd\textsubscript{12}, which has a magnetic moment of 2\(\mu\)B. The major difference in the variation of the magnetic moments of MPd and MPd\textsubscript{12} clusters is observed for Ti, V and Cr.

The local spin moments of MPd\textsubscript{12} clusters have been obtained by expanding the wave function into angular momentum components within a sphere of radius. For Pd\textsubscript{13}, the average magnetic moment on each site is 0.61\(\mu\)B. This average magnetic moment decreases significantly on substitution of central atom with V, Ti, and Cr which are coupled to the Pd\textsubscript{12} antiferromagnetically. Unlike this trend, the substitution by Mn, Fe, Co, results in the enhancement of the moment through ferromagnetic coupling.

From the charge distribution analysis it is found, that for M-Pd dimer, there is a transfer of charge to the 5s orbital of Palladium from the 4s- orbital of the heteroatom and the 4d-orbital of Pd itself. Similar trend was found in case of MPd\textsubscript{12}, the central heteroatom gives the charge to Pd\textsubscript{12} super atom. In Fig. 3 we have plotted the decomposed density of states for MnPd\textsubscript{12} and CrPd\textsubscript{12} clusters. The dashed vertical line is representing the HOMO level. It is clear from this figure, that at the HOMO energy level, while the Mn impurity atom interacts through up-spin, the Cr interacts...
behavior could be due to the hybridization of atomic s and d states. During cluster formation there is significant de-localization of 5s and 4d electrons, which leads to depletion of local d contribution around each atom and an open-shell-like behavior. Doping of Pd$_{12}$ cluster with 3d elements can lead to decrease or increase in the magnetic moments of MPd$_{12}$ cluster depending on, the electronic configuration of M element. The magnetic moment present at Ti, V and Cr atoms interacts anti-ferromagnetically with Pd$_{12}$ magnetic moment. Unlike this the magnetic moment of Mn, Fe, Co, Ni, interacts ferromagnetically. While MnPd$_{12}$ shows the highest magnetic moment of 11µB, Cr doping leads to the quenching of the magnetic moment down to 2µB.

**References**


**Conclusion**

Based on these results, we infer that, although Pd metal as bulk is non-magnetic, it can show large Magnetic Moment for finite size clusters. The reason for such through down-spin. This feature directly corroborates the ferro- and antiferro-coupling of MnPd$_{12}$ and CrPd$_{12}$ clusters, respectively as predicted above.
Mr. Sandeep Nigam joined Bhabha Atomic Research Centre in 2003 after graduating through 46th batch of training school. Since then, he has been working on theoretical study of small atomic and mixed clusters using first principal calculations. At present he is working on magnetic properties of metal encapsulated cage like clusters.

Dr Chiranjib Majumder joined Chemistry Division, Bhabha Atomic Research Centre in 1992 after graduating through 35th batch of training school. He has developed an in-house experimental facility to generate supersonic molecular beams in tandem with a time-of-flight mass spectrometer. He received his Ph.D. degree in 2000 for experimental and theoretical studies of metal clusters. During 2000-2002, he was at the Institute for Materials Research, Tohoku University, Japan to carry out post doctoral work with Prof. Y. Kawazoe, where he worked on the theoretical aspects of molecular electronics. Subsequently, he visited laboratory of Prof. P. Jena, at the Physics department of Virginia Commonwealth University, USA to work on the electronic and atomic structures of clusters. His current research interest is to design novel materials for catalysis by tuning the electronic properties of nano-materials and to underscore the mechanism of cluster-molecule interactions on a support matrix.

Dr S. K. Kulshreshtha graduated from Agra University in 1966 and joined chemistry division, BARC through 10th batch of training school. He started his research career with the study of diamagnetically substituted spinel ferrites using Mossbauer spectroscopy for which he was awarded Ph.D. by Bombay University in 1974. He did his postdoctoral work in Germany at the University of Erlangen-Nurnberg on the nature of low and high spin state transition in Fe(II) complexes. He superannuated in Dec.2006 as Associate Director Chemistry Group and Head Chemistry Division of BARC and as Outstanding Scientist. During the past 40 years, he was mainly associated with a variety of research, developmental and academic activities pertaining to the Department of Atomic Energy. Currently, Dr Kulshreshtha is working as the Adjunct Professor, Applied Chemistry Department, University Institute of Chemical Technology, Mumbai University. His current research interests are centered around material science, catalysis and structural science.