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Detailed Terms
Ab initio study of structural stability of small 3d late transition metal clusters: Interplay of magnetization and hybridization

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Using first-principles density-functional-theory–based calculations, we analyze the structural stability of small clusters of 3d late transition metals. We consider the relative stability of the two structures: layer-like structures with hexagonal closed packed stacking and more compact structures of icosahedral symmetry. We find that the Co clusters show an unusual stability in hexagonal symmetry compared to the small clusters of other members, which are found to stabilize in icosahedral-symmetry–based structure. Our study reveals that this is driven by the interplay between the magnetic-energy gain and the gain in covalency through the s-d hybridization effect. Although we have focused our study primarily on clusters with 19 atoms, we find this behavior to be general for clusters with between 15 and 20 atoms.

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I. INTRODUCTION

Atomic clusters of nanometer size have attracted special attention in present-day research due to their applications in the fields of optoelectronics,1,2 catalysis,3,4 data storage,5 sensors,6–9 etc. The first step in the theoretical study of the properties of clusters is the determination of the minimum-energy structures. The equilibrium minimum-energy structures of small clusters often prefer compact geometries10 like icosahedral- or cub-octahedral-symmetry–based structures. It has also been found in several cases that the deformed three-dimensional sections of the face centered cubic (fcc) or hexagonal closed packed (hcp) lattice appear as degenerate energy states or closely lying isomers.11 However, depending on the local symmetry, they exhibit profoundly different properties. For example, planner gold clusters exhibit outstanding catalytic activity compared to their bulk counterpart of fcc symmetry,12 and bilayer Ru nanoclusters exhibit significant chemical activity toward H2O splitting compared to Ru clusters of hcp symmetry.13 Similarly, the dependence of magnetic behavior of the Pd clusters on cluster symmetry is found to be significant.14 All of these results indicate that the determination of the local symmetry is an unavoidable part in a cluster calculation.

In this article, we present a first-principles–based analysis to understand the structural trend of transition-metal clusters. Transition-metal clusters demand special attention because of their fascinating magnetic properties,15,16 the dependence of their equilibrium structure on magnetism,17 as well as their potential biomedical applications.18–20 We focus our attention only on the 3d late-transition-metal clusters. Among the 3d late-transition-metal elements, Mn has a half-filled d level, while the others have a more than half-filled d level. Considering the earlier studies on structure of the 3d late-transition-metal clusters, it is seen that the small Mn and Fe clusters generally prefer a compact icosahedral growth pattern, as has been shown by first-principles calculations for Mn clusters21–25 and Fe clusters.26–30 For relatively less-magnetic Ni clusters and nonmagnetic Cu clusters, first-principles calculations and also some experimental evidence indicate mainly the icosahedral growth pattern.30–34,35–40 Some recent calculations41–43 also highlight the nonicosahedral or the amorphous structural pattern for small clusters of coinage metals like Cu, Ag, and Au. On the other hand, the ferromagnetic small cobalt cluster is quite different from the other members of the 3d late-transition-metal series, particularly Mn and Fe clusters. The small Coa clusters rather prefer relatively noncompact layer-like structures. In our recent work44 using first-principles density functional theory, we showed a clear hexagonal growth pattern for small Coa clusters (15 ≤ n ≤ 20). Hexagonal-symmetry–based structures in this size range consist of three planes with hcp stacking. Also recently, this layer-like structure of small Coa clusters (13 ≤ n ≤ 23) was reported by Gong et al.45,46 using density functional calculations. However, experimental work on small Coa clusters (n < 50)47–49 is unable to give any definitive conclusion, which also indicates nonicosahedral packing.

It is therefore curious why the small cobalt clusters prefer an hcp growth pattern with layer-like stacking, while the clusters of the other 3d late-transition-metal elements apparently prefer a more compact icosahedral growth pattern. In order to gain an understanding of this issue, we choose these two close-packed structures with hcp and icosahedral symmetries as starting guesses and allow them to relax under the assumption of collinear magnetic ordering. We have studied the relative stability between these two symmetry-based structures in terms of energetics and structural and electronic properties. We have carried out our study for the entire series of 3d late-transition-metal clusters (i.e., Mn1, Fe2, Co3, Ni4, and Cu5). Our study reveals that the contrasting behavior of the stability of Co clusters compared to the other members arises due to the interesting interplay of the effects of magnetization and hybridization.

II. COMPUTATIONAL DETAILS

We employed density functional theory with the plane-wave pseudopotential method as implemented in the Vienna ab initio simulation package.50 We used the projected augmented
to determine the minimum-energy structure for each competing structural symmetries have been considered in this work. These two properties of the clusters more general, we have chosen the hexagonal and icosahedral structures for 19-atom clusters and have optimized them. In the second step, we have randomly displaced a few atoms in the optimized structure obtained in the first step and have re-optimized to get the “final optimized” structure. The second step has been carried out considering all possible collinear spin arrangements of the atomic spins in each $X_{19}$ ($X = \text{Mn, Fe, Co, Ni, Cu}$) cluster within the spin-polarized calculation. The optimized clusters do not have perfect hexagonal or icosahedral symmetry but are heavily distorted.

First, to analyze the optimized structures, we define the average nearest-neighbor bond length as \( r = \frac{1}{n_b} \sum_{i>j} r_{ij} \), where \( r_{ij} \) is the bond distance between the \( j \)th and \( i \)th atoms and \( n_b \) is the number of such bonds. In the cluster calculation, we considered that the two atoms are bonded if their interatomic distance is within 2.75 Å, which is larger than any of the nearest-neighbor bulk bond lengths of these 3$d$ late-transition-metal elements. Figure 2 shows the plot of the average nearest-neighbor bond-lengths of the optimized structures of $X_{19}$ clusters for both symmetries. It is seen that the average nearest-neighbor bond lengths for the hcp structures are consistently smaller than those of the icosahedral counterpart, in agreement with the previous study, which indicates that the net attraction of nucleus on outer shell electrons is effectively greater for the hcp-symmetry–based structure. As the $d$ shell gets filled one by one with electrons from Mn $\rightarrow$ Fe $\rightarrow$ Co $\rightarrow$ Ni $\rightarrow$ Cu, the ion-electron interaction gets stronger, which increases the binding. On the other hand, electron-electron repulsion also increases, which starts to downplay the gain in electron-ion attraction. On top of this effect, the increased atom-centered magnetic moments also play a significant role, especially for the members left of Co along Co$_{19}$ to Fe$_{19}$ to Mn$_{19}$.

In Fig. 3, we show the average coordination number plotted for the optimized structures of $X_{19}$ clusters in both symmetries.

FIG. 1. (Color online) Cluster structures of 19 atoms with (a) hexagonal closed packed and (b) icosahedral symmetries. These two competing structural symmetries have been considered in this work to determine the minimum-energy structure for each $X_{19}$ cluster; $X = \text{Mn, Fe, Co, Ni, and Cu}$. 

![FIG. 1](image1.png)
We find the average coordination for hcp-symmetry–based structures to be systematically less than that of icosahedral-symmetry–based structure, giving rise to a more open geometry, although the average bond length is smaller for hcp-based structures compared with icosahedral structures (cf. Fig. 2).

The binding energy for each \(X_{19}\) cluster is calculated as 
\[E_B(X_{19}) = [19E(X) - E(X_{19})],\]
where \(E(X)\) and \(E(X_{19})\) are the total energy of an isolated \(X\) atom and that of an \(X_{19}\) cluster, respectively. In such a definition, a positive sign in \(E_B\) corresponds to binding. Table I shows the total binding energy and the total magnetic moment of the optimized hcp and icosahedral structures of each \(X_{19}\) cluster. It is seen that the icosahedral-symmetry–based structure is more stable than the hcp-symmetry–based structure for \(Mn_{19}\) and \(Fe_{19}\) clusters. Conversely, the hcp-symmetry–based structure is energetically more favorable than the icosahedral structure for the \(Co_{19}\) cluster, while both structures are almost degenerate for the \(Ni_{19}\) and \(Cu_{19}\) clusters within the accuracy of our calculations.

By analyzing the atomic spin orientations in the optimized structures of both symmetries of each \(X_{19}\) cluster, we found that the \(Mn\)-\(Mn\) interactions within the \(Mn_{19}\) cluster are mostly antiferromagnetic for both the optimal hcp and optimal icosahedral phases, as mentioned in earlier works.\(^{21,24}\) On the other hand, each of the \(Fe_{19}\), \(Co_{19}\), and \(Ni_{19}\) clusters is ferromagnetic for either of the two structural symmetries, with decreasing total magnetic moment because the atom-centered magnetic moments decrease as one goes along \(Fe_{19} \rightarrow Co_{19} \rightarrow Ni_{19}\). Figure 4 shows the distribution of atomic magnetic moments of each of the \(X_{19}\) clusters derived from both symmetries together with the corresponding optimized structures. Note that bulk \(Mn\) is also antiferromagnetic and bulk \(Fe\), \(Co\), and \(Ni\) are ferromagnetic (with a magnetic moment per atom of \(2.2\mu_B\) for \(Fe\),\(^{55,56}\) \(1.72\mu_B\) for \(Co\),\(^{56}\) and \(0.616\mu_B\) for \(Ni\)).\(^{57}\) The \(Cu_{19}\) cluster is found to be nonmagnetic with zero magnetic moment.

To have a visual representation, we plot the binding energy per atom for the optimal hcp and optimal icosahedral symmetries of each \(X_{19}\) cluster in Fig. 5. To understand the effect of magnetism on stability, we have also performed the non-spin-polarized calculation for each \(X_{19}\) cluster. The binding energies for the optimal hcp and icosahedral structures of \(X_{19}\) clusters in the non-spin-polarized calculation are also shown in Fig. 5 (right panel) with shaded bars. Interestingly, the non-spin-polarized calculation shows that the \(Mn_{19}\), \(Fe_{19}\), and \(Co_{19}\) clusters all stabilize in hcp-symmetry–based structures,
while both the structures are again degenerate for Ni_{19} and Cu_{19} clusters. From Fig. 5, it is also clearly seen that the magnetic phase always has the higher binding energy for both structures of each X_{19} cluster, indicating that the magnetic phase is the stable phase for both structures. Only in case of the Cu_{19} cluster is the binding energy of each structure the same for both the spin-polarized as well as the non-spin-polarized calculation, indicating that the Cu_{19} cluster is nonmagnetic. From the binding energy plot, we therefore conclude that the magnetism switches the stable phase from hcp to icosahedron in the case of the Mn_{19} and Fe_{19} clusters, while the magnetism further enhances the stability of the hcp phase for the Co_{19} cluster. For the Ni_{19} and Cu_{19} clusters, the effect of magnetism is small and both the hcp- as well as the icosahedral-symmetry–based structures are almost degenerate for both the spin-polarized as well as the non-spin-polarized calculations.

For Mn clusters, the effect of noncollinearity has been discussed in literature. Manganese is prone to noncollinearity due to the presence of the competing nature of magnetic interactions, although the degree of noncollinearity is found to decrease for cluster sizes larger than 13 atoms. For Fe and Co clusters, the degree of noncollinearity is reported to be smaller yet compared to Mn. Noncollinearity is favored by the magnetic energy associated with larger magnetic moments, which competes with chemical bonding energy. One would therefore expect a reduction of noncollinearity in moving to larger cluster size as well as in moving from Mn to Fe and Co. However, in order to check the influence of the possible noncollinearity which may arise due to competing magnetic interactions as well as the orbital component of the magnetic moment [driven by spin-orbit (SO) coupling], we have repeated our calculations for Fe_{19} and Co_{19} clusters in terms of GGA + SO calculations. The results obtained indicate that Fe_{19} and Co_{19} clusters are essentially collinear, with the degree of noncollinearity being less than 1°, in agreement with previously reported results. Although the orbital components of magnetism are found to be finite (≈0.08 μ_B), importantly the calculations carried out considering noncollinearity lead to only small changes in the binding-energy differences of the icosahedral and hexagonal geometries by 1%–2%, keeping the main conclusion of our study unchanged. In the following, we focus primarily on Fe_{19} and Co_{19} clusters, for which the switching of the stable phase between hcp and icosahedral structures occurs.

It is important to note that the trend in binding-energy calculation is very robust, being independent of the type of pseudopotential or of the nature of the exchange-correlation functional used in this study. We also found that this trend is general for clusters having sizes 15 ≤ n ≤ 20. The structures for n = 15, 16, 17, 18, and 20 were obtained by removing or adding atoms from the optimal 19-atom-cluster structure and then letting them optimize for all possible collinear spin configurations of the constituent atoms. In Fig. 6, we have shown a plot of binding energies of the optimal hcp and the optimal icosahedral structures of the Fe_n and Co_n clusters considering clusters sizes in the range 15 ≤ n ≤ 20. It clearly indicates that the icosahedral growth pattern is more favorable for small Fe_n clusters and that the hcp growth pattern is more favorable for the small Co_n clusters in the spin-polarized calculations, in agreement with the trend observed for 19-atom clusters and discussed above. In Table II, we have also shown our estimated magnetic moments of the optimized hcp and icosahedral structures of Fe_n and Co_n clusters in this size range. Notice that our estimated magnetic moments for the optimized structures are in fair agreement with the recent result of Stern-Gerlach experiments for Fe clusters and Co clusters.

In order to understand the optimal structures and the distortions in the structure that arise during the optimization procedure, we list in Table III the root-mean-square (rms) distortion of the bond lengths in the optimized geometries,
which gives us a feel of the distortions that accompany optimization.

The pertinent question, therefore, is what drives this phenomenon? To see the effect of magnetism, we first calculated the magnetic energy which is defined as the energy difference between the magnetic (spin-polarized) and nonmagnetic (non-spin-polarized) calculations for each of the hcp and icosahedral structures of \( X_{19} \) clusters, which were estimated for their optimal structures in magnetic and nonmagnetic calculations. Figure 7(a) shows the plot of magnetic energies of the \( X_{19} \) clusters for hcp- and icosahedral-symmetry–based optimal structures. It is interesting to note that the magnetic energy of the icosahedral structure is much higher than that of the hcp-symmetry–based structure for the \( X_{19} \) clusters (and also for the \( Mn_{19} \) cluster, although we do not bring it into our discussion due to the assumption of collinearity in our calculation, as mentioned before). On the other hand, it is of similar magnitude for the hcp-symmetry–based structure for the \( Mn_{19} \) cluster and its icosahedral counterpart, with hcp being somewhat higher. The magnetic-energy difference between hcp and icosahedral structures is negligibly small in case of the \( Ni_{19} \) and \( Cu_{19} \) clusters. The zoomed plot around the \( Fe_{19} \) and \( Co_{19} \) datum points in Fig. 7(b) shows the effect of magnetism more clearly. We note that the difference of magnetic-energy gains between the hcp and icosahedral structures in the case of the \( Co_{19} \) cluster is relatively small compared to that of the \( Fe_{19} \) cluster. As the \( d \) shell gets progressively filled up starting from the half-filled situation with the highest atom-centered magnetic moment for the \( Mn_{n} \) cluster, the magnetic-energy gain gets progressively weaker, so the role of magnetism is more important for \( Fe \) compared to \( Co \).

In order to understand the gain in magnetic energy for the icosahedral structure of the \( Fe_{19} \) cluster and for the hcp structure of the \( Co_{19} \) cluster, we have studied the density of states (DOS) of the optimized hcp and icosahedral structures of the \( Fe_{19} \) and \( Co_{19} \) clusters for both the magnetic and nonmagnetic calculations, as shown in Fig. 8. We note that, compared to the nonmagnetic DOS, the gap in the majority-spin channel is significantly enhanced in case of the icosahedral structure of \( Fe_{19} \) and the hcp structure of \( Co_{19} \), indicating their enhanced stability. On the other hand, for the optimal hcp structure of \( Fe_{19} \) and for the optimal icosahedral structure of \( Co_{19} \) clusters in case of the spin-polarized calculation, there is a finite number of states around the Fermi energy, which reduces the stability of the system compared to that of the corresponding icosahedral and hcp structures.

We next study another relevant quantity which has been used previously to examine the relative stability between the various classes of isomers for 3d late-transition-metal clusters; namely, the hybridization of the atomic 3d and 4s orbitals. The \( s-d \) hybridization index as quantified by H"akkinen et al.\textsuperscript{53} and later used by Chang et al.\textsuperscript{54} as well as Wang et al.\textsuperscript{64} for transition-metal clusters is defined for a 19-atom cluster as

\[
H_{sd} = \sum_{I=1}^{19} \sum_{i,s} w_{i,s}^{(I)} w_{i,d}^{(I)}
\]

where \( w_{i,s}^{(I)} (w_{i,d}^{(I)}) \) is the projection of \( i \)th Khon-Sham orbital onto the \( s \) (\( d \)) spherical harmonic centered at atom \( I \), integrated over a sphere of specified radius. The spin index is implicit in the summation. Our calculated \( s-d \) hybridization index for the optimized structures of both the symmetries for the \( Fe_{19} \) and \( Co_{19} \) and also for the \( Ni_{19} \) and \( Cu_{19} \) clusters have been plotted in Fig. 9. To see the effect of magnetism, we have studied the \( s-d \) hybridization of the optimized structure of each cluster for both the magnetic and nonmagnetic phases.

It is seen that the optimized hcp structures have consistently higher values of \( H_{sd} \) than those of the optimized icosahedral structures of 3d late-transition-metal clusters \( X_{19} \) for both

\[
\begin{array}{cccc}
\text{Clusters} & \text{hcp} & \text{icosa} & \text{Expt.} \\
\hline
\text{Fe}_{19} & 3.07 & 3.20 & 2.72 \\
\text{Fe}_{18} & 3.13 & 3.13 & 2.94 \\
\text{Fe}_{17} & 3.18 & 3.06 & 2.86 \\
\text{Fe}_{16} & 3.11 & 3.11 & 3.02 \\
\text{Fe}_{15} & 3.05 & 3.05 & 2.92 \\
\text{Fe}_{20} & 3.00 & 3.00 & 2.73 \\
\hline
\text{Co}_{19} & 2.07 & 1.93 & 2.38 \\
\text{Co}_{18} & 2.13 & 1.88 & 2.53 \\
\text{Co}_{17} & 2.06 & 2.06 & 2.24 \\
\text{Co}_{16} & 2.00 & 2.00 & 2.07 \\
\text{Co}_{15} & 2.05 & 1.95 & 2.21 \\
\text{Co}_{20} & 2.00 & 1.90 & 2.04 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Clusters} & \text{hcp} & \text{icosa} & \text{Expt.} \\
\hline
\text{Mn}_{19} & 3.00 & 3.00 & 2.73 \\
\text{Fe}_{19} & 2.07 & 1.93 & 2.38 \\
\text{Co}_{19} & 2.13 & 1.88 & 2.53 \\
\text{Fe}_{18} & 2.06 & 2.06 & 2.24 \\
\text{Co}_{18} & 2.00 & 2.00 & 2.07 \\
\text{Fe}_{17} & 2.05 & 1.95 & 2.21 \\
\text{Co}_{17} & 2.00 & 1.90 & 2.04 \\
\text{Fe}_{16} & 3.07 & 3.20 & 2.72 \\
\text{Co}_{16} & 2.07 & 1.93 & 2.38 \\
\text{Fe}_{15} & 2.13 & 1.88 & 2.53 \\
\text{Co}_{15} & 2.06 & 2.06 & 2.24 \\
\text{Fe}_{14} & 2.00 & 2.00 & 2.07 \\
\text{Co}_{14} & 2.05 & 1.95 & 2.21 \\
\text{Fe}_{20} & 3.00 & 3.00 & 2.73 \\
\text{Co}_{20} & 2.00 & 1.90 & 2.04 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Clusters} & \text{hcp} & \text{icosa} & \text{Expt.} \\
\hline
\text{Fe}_{19} & 0.100 & 0.075 \\
\text{Fe}_{18} & 0.125 & 0.083 \\
\text{Fe}_{17} & 0.129 & 0.076 \\
\text{Fe}_{16} & 0.113 & 0.089 \\
\text{Fe}_{15} & 0.121 & 0.096 \\
\text{Fe}_{20} & 0.123 & 0.095 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Clusters} & \text{hcp} & \text{icosa} & \text{Expt.} \\
\hline
\text{Co}_{19} & 0.046 & 0.118 \\
\text{Co}_{18} & 0.043 & 0.073 \\
\text{Co}_{17} & 0.036 & 0.073 \\
\text{Co}_{16} & 0.058 & 0.077 \\
\text{Co}_{15} & 0.054 & 0.110 \\
\text{Co}_{20} & 0.072 & 0.087 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Clusters} & \text{hcp} & \text{icosa} & \text{Expt.} \\
\hline
\text{Ni}_{19} & 0.113 & 0.089 \\
\text{Ni}_{18} & 0.121 & 0.096 \\
\text{Ni}_{17} & 0.129 & 0.076 \\
\text{Ni}_{16} & 0.113 & 0.089 \\
\text{Ni}_{15} & 0.121 & 0.096 \\
\text{Ni}_{20} & 0.123 & 0.095 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Clusters} & \text{hcp} & \text{icosa} & \text{Expt.} \\
\hline
\text{Cu}_{19} & 0.054 & 0.110 \\
\text{Cu}_{18} & 0.043 & 0.073 \\
\text{Cu}_{17} & 0.036 & 0.073 \\
\text{Cu}_{16} & 0.058 & 0.077 \\
\text{Cu}_{15} & 0.054 & 0.110 \\
\text{Cu}_{20} & 0.072 & 0.087 \\
\end{array}
\]
spin-polarized and non-spin-polarized calculations. In order to see distinctly the effect of magnetization on s-d hybridization, we have plotted the difference of s-d hybridization indices between the optimized hcp and the optimized icosahedral structures for both the magnetic and nonmagnetic calculations in the right panel of Fig. 9. The positive (negative) value of this difference, $H_{sd}^{diff}$, indicates that the hcp (icosahedron) structure has higher s-d hybridization. It is clearly seen that, although the difference is positive for all the late-transition-metal clusters, it shows some variation across the series. The s-d hybridization gain in favor of the hexagonal structure is the maximum for the magnetic Co$_{19}$ cluster, showing a factor of about six-times enhancement compared to nonmagnetic Co$_{19}$. The Cu$_{19}$ cluster being essentially nonmagnetic, the s-d hybridization gain between the two structural symmetries remains the same both in the magnetic and nonmagnetic calculation of Cu$_{19}$. The s-d hybridization gain remains similar for the magnetic Fe$_{19}$ and nonmagnetic Fe$_{19}$ ($H_{sd}^{diff} \sim 0.3$) and that for magnetic Ni$_{19}$ and nonmagnetic Ni$_{19}$ ($H_{sd}^{diff} \sim 0.4$). Therefore, we conclude that the gain in s-d hybridization stabilizes the hcp-symmetry–based structure over the icosahedral-symmetry–based structure for the Co$_{19}$ cluster. This is also helped in a way by the small but positive magnetic-energy gain in favor of hcp phase of the Co$_{19}$ cluster. So the s-d hybridization helped by magnetic-energy gain stabilizes the hcp-symmetry–based structure in the case of the Co$_{19}$ cluster. On the other hand, for the Fe$_{19}$ cluster, the large magnetic-energy gain in favor of the icosahedral symmetry decides the final stability, thereby counteracting the hybridization-energy gain in favor of hexagonal symmetry.

**IV. SUMMARY AND CONCLUSIONS**

To summarize, we have investigated the relative stability of the 3d late-transition-metal clusters, especially of 19 atoms, between hcp and icosahedral symmetries. Among all the members, the Co$_{19}$ cluster prefers an unusual stabilization in hexagonal symmetry, while the rest prefer icosahedral symmetry. Our study nicely demonstrates that this curious result is driven by the interplay of the gain in magnetic energy vis-à-vis the gain in hybridization energy. For the Co$_{19}$ clusters, the hybridization-energy gain helped by magnetic-energy gain favors the stabilization of hexagonal symmetry while, for clusters like Fe$_{19}$, the large magnetic-energy gain in icosahedral symmetry topples the s-d hybridization gain in favor of hexagonal symmetry and stabilizes the icosahedral phase. We find that the trend obtained also holds good for clusters with between 15 and 20 atoms.

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