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A cluster-beam technique is used to produce nearly monodispersed nanoclusters of Co while independently varying their size and concentration. The Co clusters are embedded in Cu and SiO_2 to form films with cluster size varying from 300 to 9000 atoms and Co concentration varying from 10 to 50 vol %. The Co magnetization (M_s) increases with increasing cluster size and decreases with increasing Co concentration for a given cluster size but is always less than the bulk value. First-principles calculations are used to analyze the experimental data in terms of the local environment effects at the cluster-matrix interface and spin-glass-like behavior due to the strong ferro- and antiferromagnetic intercluster exchange interactions for small separations.

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I. INTRODUCTION

Magnetic nanostructures consisting of clusters, dots, wires, and arrays are of considerable interest at present for several reasons. They exhibit novel properties such as switching behavior that is controllable via feature dimensions and separations. They also are essential for advances in technologies such as high-density data storage, spin electronics, memory devices, and high-performance magnetic materials. As characteristic lengths decrease to 10 nm and lower, fabricating and understanding the properties of magnetic nanostructures become increasingly difficult. Emerging techniques such as cluster-beam synthesis of nanostructured materials,[1,2] electrodeposition of nanodots or wires into self-assembled templates,[3,4] and nanoimprint lithography[5,6] are capable of fabricating novel nanostructures. A few theoretical calculations have been reported for a magnetic cluster embedded in a nonmagnetic medium.[7] However, no systematic experimental studies and first-principle calculations of cluster moments and interactions in cluster-assembled materials have been reported so far.

In this paper we present the first combined experimental and theoretical study of nearly monodispersed magnetic clusters (Co) embedded in a host matrix (Cu or SiO_2). In many studies of magnetic nanoparticles, a broad distribution of particle sizes and shapes made the interpretation of results difficult. In the present study, Co cluster-assembled materials are made by a cluster-deposition system with relatively uniform cluster sizes, and thus the results are not subject to this limitation. Recent work of Jamet *et al.* was aimed at probing the magnetic anisotropy of a single Co nanocluster and the interface magnetic anisotropy in Co clusters embedded in a Nb matrix.[8] The Co clusters were embedded in a Nb matrix and it was estimated that there are two magnetically dead monolayers of Co at the surface of the clusters. This is consistent with the miscibility of Co and Nb. The present study is focused mainly on Co clusters in a Cu matrix because Co and Cu are *immiscible* in the bulk (though there is some miscibility at surface layers[9]); thus it might be anticipated that such interface effects would be considerably smaller (but they are not as will be seen later). First-principle studies are carried out for the magnetization of a single cluster and intercluster exchange interactions in order to analyze the experimental data.

II. EXPERIMENT AND RESULTS

Co clusters of a variable mean size of about 300–9000 atoms are generated by combining an improved magnetron-sputtering source with a gas-aggregation tube at liquid nitrogen temperature.[10–14] The clusters land softly on the surface of a Si (100) substrate at room temperature simultaneously along with an atomic beam of Cu or SiO_2 from a magnetron-sputtering gun. This results in the embedding of Co clusters in a Cu or SiO_2 matrix.[14,15] The cluster concentration is adjusted through the ratio of the cluster and atomic-beam deposition rates, as measured *in situ* with a quartz microbalance. The cluster-size distribution is monitored *in situ* by time-of-flight measurements, and checked by transmission electron microscopy. The distribution fits well to a lognormal function with a narrow size distribution, typically $\sigma_d/\bar{d} \approx 0.12$, where σ_d and $\bar{d}$ are the rms deviation and mean diameter of clusters, respectively. Samples were made with Co volume concentrations of 10% to 50%. All the samples were approximately 35 nm thick and capped with 3 nm of matrix material to allow sample transfer in the atmosphere. Figure 1(a) shows a high-resolution transmission-electron-microscopy (HRTEM) image of a Co_{9000} cluster ($d = 6.2$ nm) at 10% concentration in Cu. It can be seen there is some interface diffusion around the Co cluster. Figure 1(b) is a nanodiffraction pattern from the Co cluster. Comparing with the simulations of face-centered-cubic (FCC) and hexagonal-close-packed (HCP) structure models, the pattern shows a typical fcc structure.

For all the samples, we measured the magnetization versus applied field [$M(H)$] at 5 and 300 K by superconducting quantum interference device magnetometry. The maximum measuring field is 55 kOe. All the samples at room temperature are superparamagnetic except the 9000 atom clusters at 50%. At 5 K, they are magnetically ordered with hysteresis

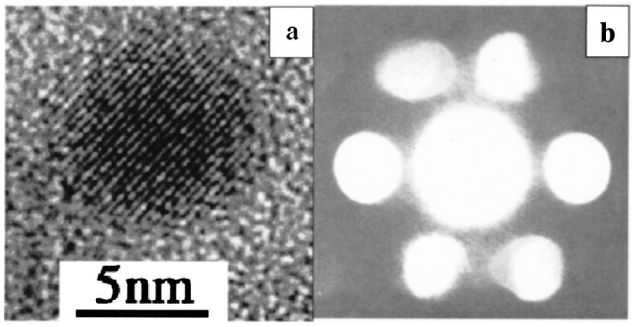

FIG. 1. HRTEM image and nanodiffraction pattern on Co nanoclusters. (a) A Co_{9000} cluster ($d=6.2$ nm) in Cu, (b) a [110] zone axis nanodiffraction pattern from the Co cluster. The pattern shows a typical FCC structure.

loops. The loops obtained at 5 K after cooling in various fields did not show any field shift that would indicate an exchange bias phenomenon from a CoO shell magnetically coupled to the Co cluster core. This means the films were not significantly oxidized.

Figure 2 shows the results of magnetization per unit volume of Co (M_s) as a function of Co concentration in a matrix at 5 K for several cluster sizes. M_s was obtained by high-field fits to the expression $M=M_s(1-A/H^2)$, where A is a constant. It can be seen that M_s increases as one goes from (300–1000)-atom clusters to (4500–9000)-atom clusters. As expected, 9000-atom clusters have higher M_s in an insulating matrix (SiO_2) than in a metallic matrix (Cu). Also, M_s decreases with increasing Co concentration for all cluster sizes. Finally, the magnetization for clusters is always lower than the bulk Co value.

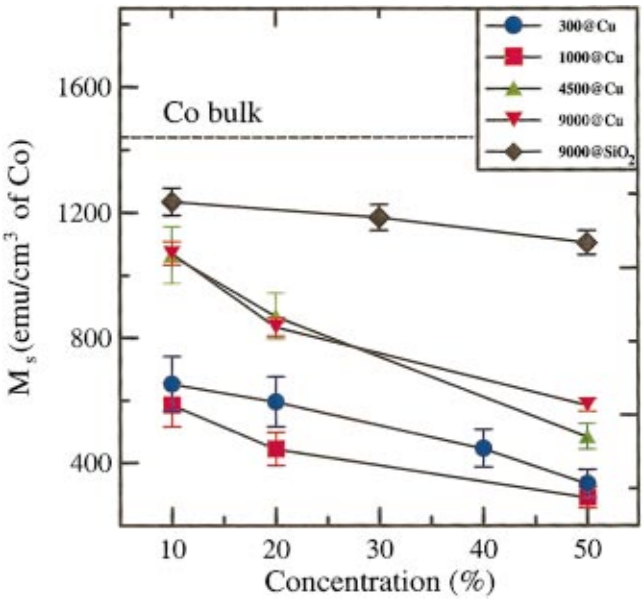

FIG. 2. (Color). Magnetization per unit volume of Co as a function of Co concentration with the different cluster sizes and matrices at 5 K.

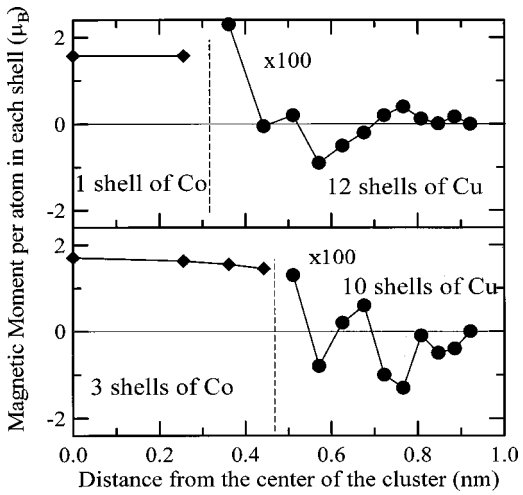

FIG. 3. Calculated magnetic moments per Co (diamond) and Cu atoms (circles, magnified 100 times) as a function of the distance from the center of a cluster, for one- and three-shell Co clusters.

III. CALCULATIONS AND DISCUSSION

In order to gain some theoretical understanding of the experimental data, we have performed self-consistent spin-polarized electronic structure calculations for substitutional Co clusters in the Cu matrix (fcc structure) using the tight-binding linear-muffin-tin-orbital and recursion methods.[16] Total energy variation calculations are based on Harris-Foulkes approach.[17] The cluster size is increased by adding complete successive shells of Co atoms surrounding the central Co atom. The first shell has twelve atoms, the second six, etc., in a fcc lattice. We consider thirteen clusters with the number of Co atoms ranging from 13 to 321. To investigate the sensitivity of the Co moment to its local environment, calculations are also carried out for a single impurity and a nearest-neighbor pair. The electronic structure results are used to calculate M_s as a function of the size of the cluster.

We find that a single substitutional Co impurity is not magnetic if relaxation of the first two shells of Cu neighbors is taken into account (in an unrelaxed Cu matrix, Co has a moment of $0.83\mu_B$). This is in agreement with the experimental data in Ref. 18. The inward relaxation of the first and second shell, based on total energy calculations, is 1% and 0.5%, respectively. Thus the Co moment is very sensitive to the changes in its hybridization with the surrounding atoms. In the case of two Co impurities as nearest neighbors the Co atoms have magnetic moment of $1.1\mu_B$. M_s as a function of the Co cluster size is calculated by adding successive shells around the single impurity. The moment per atom as a function of the distance from the center of the cluster is shown in Fig. 3 for clusters with 1 and 3 Co shells surrounding the central Co atom. We see that all finite-size clusters have Co magnetic moment comparable to the bulk Co value. The calculations were carried out for a total of 13 Co and Cu shells. The neighboring Cu shells develop very small oscillatory magnetic moments making negligible contribution to the overall magnetization.

The theoretical calculations described above for the ideal clusters give the average magnetic moment per Co atom to

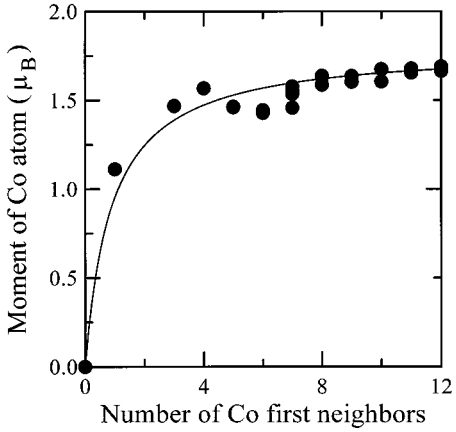

FIG. 4. Calculated magnetic moment of Co atoms as a function of the number of Co atoms as nearest neighbors. The multiple values of the moments in some cases are due to the different Co neighbor configurations at various cluster surfaces.

be of the order of the bulk value ($1.7\mu_B$), almost independent of the size of the cluster. On the other hand the experimental data in Fig. 2 show that the average magnetization of a cluster is smaller than the bulk value in general and decreases with the decreasing cluster size. Since the intercluster interactions at low Co concentration are not expected to be very significant, the disagreement in this case may be related to the local-environment effects at the cluster-matrix interface in the experimental clusters. To probe this effect we calculated the moment of a Co atom as a function of the number of its Co nearest neighbors in a Cu matrix and the results are shown in Fig. 4. The first two points in Fig. 4 are for a single Co atom and Co pair in the Cu matrix, respectively, while the rest of the points are calculated results for the various atoms at the surface of the 13 clusters considered in this study. We see that the Co moment increases sharply from zero for no first-neighbor Co atoms to the bulk value for the twelve Co first neighbors. This is in qualitative agreement with the observed reduction in magnetization of a metastable Cu(Co) alloy with increasing Cu concentration.[18,19] Such moment reduction and noncollinear ordering due to local-environment effects at the cluster-matrix interface must be responsible for the experimentally observed reduction in magnetization. Shan *et al.*[20] showed for Co/Cu multilayers that there was an interface Co layer of thickness about 1.2 Å that had no moment, presumably due to intermixing at the interface. If we assume that all of the Co atoms at the surface of an ideal cluster do not contribute to the magnetization due to the interface effects we can calculate the magnetization per cluster. The remaining central or core Co atoms have the bulk moment value. Using this procedure we have calculated the average magnetic moment per Co atom for clusters up to 10 000 atoms. The results are compared with the experimental data for 10% Co concentration in Fig. 5. We see that the agreement between theory and experiment is quite reasonable for low Co concentration. Also it can be seen from Fig. 5 that the fraction of Co atoms that lose their moments is quite large for smaller clusters but decreases rapidly with increasing cluster size. The small oscillations in the calculated curve are related to the discontinuous changes in the number of core and surface Co atoms with the addition of each successive shell to the cluster. Such an oscillatory behavior has been observed in free clusters.[21]

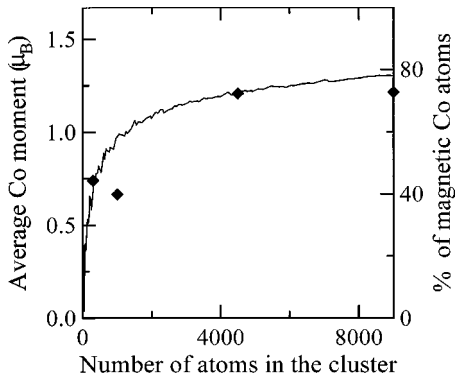

FIG. 5. The average magnetic moment per Co atom and the percentage of magnetic Co atoms as a function of the cluster size. The points are experimental data for 10% Co concentration.

Next we consider the decrease in M_s with increasing Co concentration for a given cluster size as well as the previously observed spin-glass-like transitions (susceptibility peaks) of the magnetization.[15] These effects are related to the intercluster interactions. The intercluster exchange parameters strongly depend on the shape and size of the clusters as well as their separation. It is extremely difficult to determine a parametric description of the shape and size dependence of the intercluster exchange coupling. Some qualitative understanding can be obtained using a computationally manageable size of the cluster. We have calculated the exchange interaction J_{ij} between two 141-atom clusters (8 shells) as a function of their separation in a Cu matrix. The results of the first-principles calculations are shown in Fig. 6. Figure 6 also shows a Ruderman-Kittel-Kasuya-Yosida (RKKY) function based on Cu Fermi momentum $k_f = 1.358\ \mathrm{A}^{-1}$. The calculated results do not appear to be RKKY-type for smaller separations between the clusters. They are expected to become RKKY type for larger separations.[22] Of necessity the number of separations of the two clusters is limited; thus there are not enough calculated points to be more specific about the parametric description of the intercluster exchange

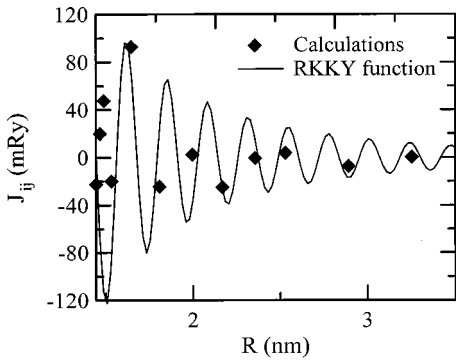

FIG. 6. Exchange coupling between Co clusters as a function of intercluster separation: the results presented for two 141-atom clusters embedded in Cu matrix. The solid curve corresponds to RKKY interactions with k_F of Cu ($1.358\ \mathrm{A}^{-1}$).

interactions. The ferro-and antiferromagnetic J_{ij} for separation less than 2.5 nm are relatively large, i.e., of the order of the interatomic J_{ij} of bulk Co values and dominate over the magnetostatic interactions. Such exchange interactions will produce noncollinear or spin-glass-like ordering of random distribution of moments observed experimentally for Co clusters in Cu.[15] The distance between neighboring clusters of a given size decreases with increasing Co concentration. This leads to an increase in ferro- and antiferromagnetic coupling among neighboring clusters. The consequent enhancement of spin-glass-like behavior will reduce M_s with increasing Co concentration as observed experimentally. Also it can be seen from Fig. 2 that the reduction in M_s is faster for larger clusters. This is due to the more rapid increase in spin-glass-like behavior with a faster reduction in intersurface separation of larger clusters as the Co concentration increases.

When the Co clusters are embedded in a nonmetallic matrix (SiO_2) instead of a metallic matrix (Cu), the cluster-matrix hybridization at the interface and cluster-cluster exchange interactions are reduced. As a result, the Co magnetization for a given cluster size is higher compared to the metallic matrix and the reduction in magnetization with increasing Co concentration is less pronounced.

IV. CONCLUSION

In summary, a cluster deposition system has been used to make Co clusters imbedded in Cu and SiO_2 matrices, independently varying the size and concentration of clusters. First-principle self-consistent electronic-structure calculations have been carried out to analyze the observed magnetization of Co clusters as a function of their size and concentration. These calculations along with a plausible cluster-matrix interface model give magnetization in good agreement with the data for low Co concentration. The calculated intercluster exchange interactions are used to qualitatively explain the magnetization data as a function of Co concentration and spin-glass type behavior in these systems. Detailed measurements and calculations of the type discussed here will be necessary to understand the magnetic properties of a variety of magnetic nanostructures where interface instabilities and interactions are important.

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