Ferromagnetic Stability in Fe Nanodot Assemblies on Cu(111) Induced by Indirect Coupling through the Substrate

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We report collective ferromagnetic behavior with high Curie temperatures (T_c) in Fe dot assemblies supported by the Cu(111) surface. Our ability to tune the average size and spacing of the individual dots allows us to conclude that enhanced magnetic anisotropy cannot account for this high-T_c ferromagnetic order. Because our Monte Carlo simulations have ruled out the dipolar interaction as the dominant factor in this system, we attribute the origin of the ferromagnetic order to indirect exchange coupling via the Cu(111) substrate.

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To first order, assemblies of nanoscale magnetic dots are superparamagnetic. In these systems, thermal energy, which causes fluctuation of the dots' magnetic moments, becomes significant enough to overcome the anisotropy energy barrier and randomize their orientation at the so-called blocking temperature. This typically occurs far below room temperature. In real nanodot assemblies, it has been generally recognized that the magnetic dipole-dipole interaction can affect the barrier height for flipping the spin of each individual dot as well as the collective magnetic behavior of the dot assembly [1–9]. Recently, in a Cu(100) surface-supported Co island assembly, long-range ferromagnetic order with a Curie temperature (T_c) of about 200 K was observed when the Co islands approached the limit of two-dimensional morphological percolation [10]. The observed ferromagnetic long-range order was interpreted as a consequence of the long-range dipolar interaction [11].

In this Letter, we report collective ferromagnetic behavior in two-dimensional Fe dot assemblies on the Cu(111) surface that persists above room temperature. Our ability to tune the average size and spacing of the dots enables us to investigate the relative contributions of the mechanisms that support this unexpectedly robust magnetic order. Our experimental results and simulations indicate that the high-T_c ferromagnetism cannot be explained by either magnetic anisotropy or the simple dipolar interaction. Therefore, the ferromagnetic order in the Fe dot assemblies is a result of an indirect exchange interaction via the Cu(111) substrate.

Direct deposition of Fe onto Cu(111) does not lead to dot formation [12–14]. Therefore, the Fe/Cu(111) dot assemblies were synthesized by a novel method known as buffer layer assisted growth (BLAG) [15] in an ultra-high vacuum (UHV) system with base pressures below 1×10^{-10} Torr. The Cu(111) single crystal surface was prepared by cycles of 1 keV Ne ion sputtering and annealing to 800 K, before it was cooled to about 15 K. Inert Xe gas of 5*N* purity was then released into the UHV chamber. Xenon exposures ranged from 0 to 600 L [1 langmuir (L) = 10^{-6} Torr s]. Iron was then evaporated from a wire (5*N* purity) that was heated by electron bombardment. The deposition rate was independently calibrated by a combination of *in situ* scanning tunneling microscopy (STM), reflection high energy electron diffraction, and Auger electron spectroscopy. After Fe deposition, the sample was slowly warmed to 300 K to desorb the Xe buffer layer and allow the Fe dots to land on the Cu substrate. *In situ* STM and magneto-optical Kerr effect (MOKE) measurements were then performed.

Fe/Cu(111) dots grown by the BLAG method are shaped like slightly flattened hemispheres with a rather random spatial distribution. Figure 1(a) shows the STM morphology of a typical Fe dot assembly formed by depositing the equivalent of 0.8 ML (monolayer) Fe (nominal thickness) assisted by 200 L Xe. The density of the dots, after a statistical analysis of images taken at various areas on the surface, is estimated to be about $8.05 \times 10^3/\mu\text{m}^2$. This yields an average dot volume of around 8.2 nm^3, i.e., ~700 Fe atoms if we assume a bcc structure. Dot profile analysis indicates that the average height and the average width of the Fe dots are 1.4 and 3.5 nm, respectively [16].

The MOKE measurements of the Fe dot assembly shown in Fig. 1(a) reveal clear ferromagnetic behavior. Figure 1(b) shows in-plane hysteresis loops of the dot assembly at various temperatures. No perpendicular magnetization can be measured even at maximal field of 2400 Oe, indicating that the Fe dots have an in-plane easy magnetization axis. The remanent magnetization

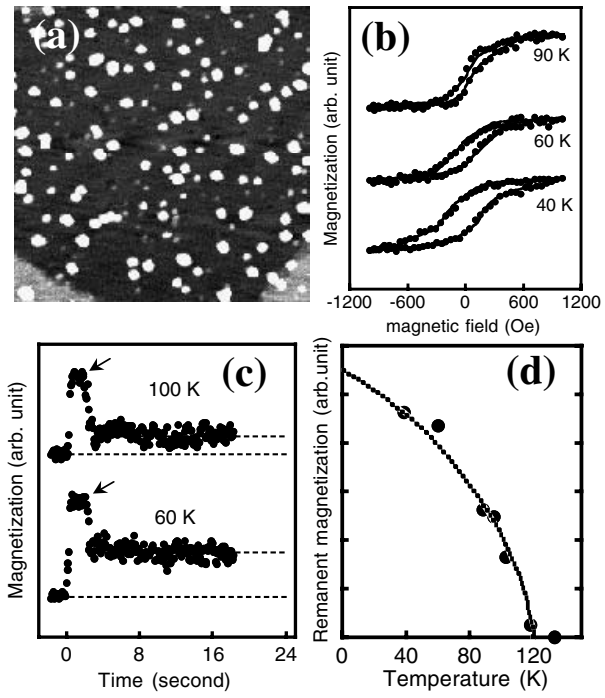

FIG. 1. (a) STM morphology (100 nm × 100 nm) of an Fe dot assembly on Cu(111) prepared with 0.8 ML Fe and 200 L Xe. (b) MOKE hysteresis loops of the Fe dot assembly at various temperatures. (c) Time dependence of the magnetization of the Fe dot assembly. An in-plane external field was applied at time "zero" and was switched off at the points in time indicated by the arrows. (d) Remanent magnetization of the Fe dot assembly as a function of temperature. The critical temperature is around 120 K.

(M_r) of the dot assembly, while strongly dependent on temperature, is remarkably stable with respect to time, as shown in Fig. 1(c). For the time-dependent magnetization measurements, the dot assembly was first demagnetized and then magnetized by an in-plane field of 2000 Oe. The external field was then removed at the point in time indicated by the arrows. The magnetization, after an initial rapid fall, remains very stable (with respect to time) even at elevated temperatures. Such stability allows us to define a meaningful critical temperature (T_c) above which M_r vanishes. As shown in Fig. 1(d), T_c of the 0.8 ML Fe/200 L Xe dot assembly is around 120 K.

This rather high T_c cannot be explained by superparamagnetic blocking if the bulk bcc Fe anisotropy (4.72×10^5 ergs/cm^3) is assumed for the Fe dots. Using the bulk anisotropy and an average volume of 8.2 nm^3, the blocking temperature of the Fe dots is estimated to be no more than 2 K. Therefore, it must be the case that the ferromagnetic stability originates from either a much larger magnetic anisotropy or from dot-dot interaction(s). To distinguish between these two factors, it is critical to be able to measure how the magnetic ordering temperature is affected when the average spacing of Fe dots is varied and the average size is fixed. A significant change of T_c would indicate that dot-dot interaction(s) play a much more dominant role than the magnetic anisotropy does, since the dot-dot interaction(s) would change with varied dot spacing, while magnetic anisotropy would not. If T_c varied little, then one would have to rule out the significance of dot-dot interactions.

We found that we could tune the average spacing and average size of the Fe dots by controlling both the Fe dosage and the Xe exposure. The effects of independently varying the Fe dosage and Xe exposure are displayed in Fig. 2. The density and the average size of the Fe dot assemblies are shown as a function of Fe dosage at a fixed Xe exposure of 200 L in 2(a), and as a function of Xe exposure at a fixed dosage of 1 ML in 2(b). Apparently, changing the Xe exposure has a more dramatic affect on the dot size and density than varying the Fe dosage. The fact that the dot size increases with increasing Xe exposure can be understood to result from the enhanced likelihood for Fe clusters to collide and stick to each other as they work their way toward the Cu surface through a thicker buffer layer. Based on the information in Fig. 2, we can find at least two sets of Fe dosage/Xe exposure parameter combinations that produce Fe dot assemblies with different densities but the same average dot size. These conditions are summarized in Table I. For example, 200 L Xe/4.5 ML Fe and 428 L Xe/1 ML Fe yield Fe dot assemblies that have identical average volume of 25 nm^3 ($\sim 2.3 \times 10^3$ atoms), but densities that differ by a factor of 5 ($1.5 \times 10^4/\mu$m^2 and $3 \times 10^3/\mu$m^2, respectively). The morphologies of these two Fe dot assemblies are shown in the upper images in Fig. 3.

The critical temperatures of the two assemblies are drastically different, despite the fact that they have the same average size. Figure 3 shows the remanent magnetization of the two dot assemblies as a function of temperature. The dot assembly (200 L Xe/4.5 ML Fe) with

TABLE I. Fe dot assemblies with equal size but different spacing.

Fe dose (ML)	Xe exposure (L)	Average volume (nm^3)	Average density (μm^{-2})	Measured T_c (K)
1.0	428	25	3.1×10^3	150
4.5	200	25	1.5×10^4	325
1	300	12	6.2×10^3	190
1.6	200	12	1.0×10^4	250

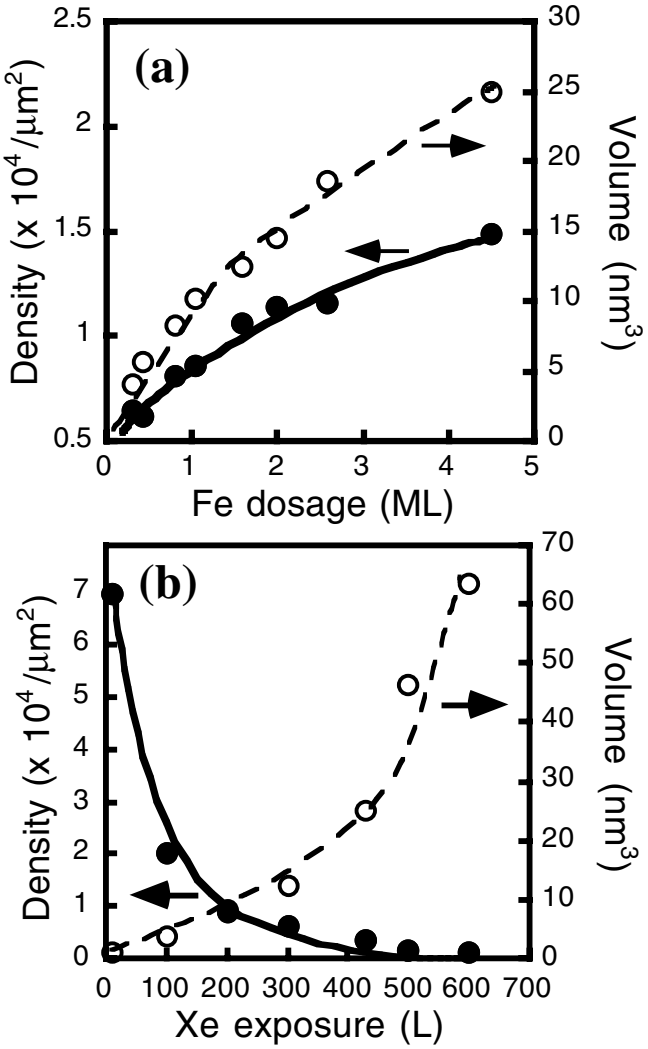

FIG. 2. Average size and density of Fe/Cu(111) dot assemblies as a function of Fe dosage (a), and Xe exposure (b). The solid and dashed lines are guides for the eyes. Two sets of Fe dosage/Xe exposure parameter combinations can produce Fe dot assemblies with different density but the same size. They are summarized in Table I.

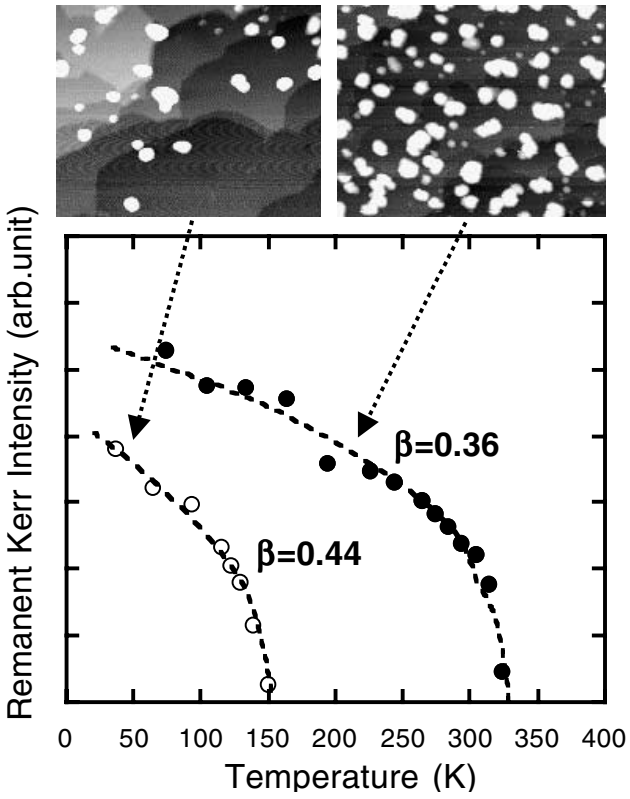

FIG. 3. Morphology and magnetization of Fe/Cu(111) dots prepared by conditions highlighted in Table I. Top: STM images (100 nm × 100 nm) of Fe/Cu(111) dots with equal average sizes (~ 25 nm^3) but different densities. Bottom: Their corresponding remanent magnetization measured as a function of temperature, with the critical exponent of power-law fitting (dashed lines) indicated.

the higher density has a T_c of about 325 K, which is more than 2 times higher than the T_c of the low-density dot assembly (~ 150 K). Similar T_c enhancement is also observed in the other pair of dot assemblies as shown in Table I. Since the contribution of the magnetic anisotropy to the thermal stability of M_r in each case should be identical, the discrepancy in T_c allows us to rule out enhanced magnetic anisotropy as the root of the high-T_c ferromagnetism. This argument is also supported by a recent observation that showed the magnetic anisotropy of Co clusters approached that of bulk Co once each cluster was large enough to contain 40 atoms [17]. Considering the fact that each Fe dot in Fig. 3 contains about 2300 atoms in average, one would expect these Fe dots to have a magnetic anisotropy close to the bulk value. If this is true, the magnetic anisotropy alone would only give rise to a blocking temperature of about 30 K, which is far below the observed T_c.

Having ruled out the role of magnetic anisotropy, the ferromagnetic stability of the Fe dot assemblies must originate from dot-dot interaction(s). The strength of the interaction is rather strong, as evidenced by the high T_c of the Fe dot assemblies. Based on the average dot size (8.2 nm^3) and density ($8.05 \times 10^3/mm^2$) in Fig. 1, we can estimate the energy scale of dipolar interaction is on the order of 2.5 K. We have further performed a Monte Carlo simulation based on the actual size and position distribution from STM experiments. The simulation showed that the dipolar interaction does not lead to a T_c higher than 20 K even assuming an Ising-like anisotropy. The dipolar interaction, however, can become significant if the spacing between the dots becomes very small, as clearly demonstrated by the work in Refs. [10,11].

Based on the aforementioned results, we conclude that a substrate-mediated, indirect exchange interaction between the Fe dots is responsible for the persistent magnetic order. To understand the exact nature of the indirect

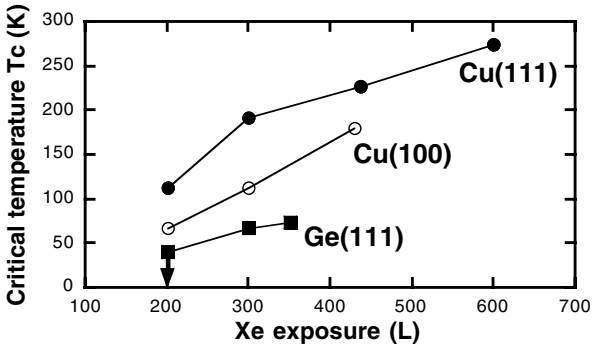

FIG. 4. Critical temperature (T_c) of Fe dot assemblies on various substrates of Cu(111), Cu(100), and Ge(111) as a function of Xe exposure. The Fe nominal thickness is fixed at 1 ML in all cases. The arrow for the Fe/Ge(111) dots (200 L Xe) indicates that the T_c is below 40 K.

exchange interaction, it is useful to compare the T_c values of Fe dot assemblies prepared under similar conditions on various substrates. Figure 4 shows T_c of Fe dot assemblies prepared on Cu(111), Cu(100), and Ge(111) as a function of Xe exposure. In all cases, the Fe nominal thickness is 1 ML. Evidently, under similar growth conditions, Fe dots consistently exhibit the highest T_c on Cu(111) and the lowest T_c on semiconducting Ge(111). This again suggests that substrate-mediated interaction dominates other factors including magnetic anisotropy (including shape anisotropy) and dipolar interaction in the Fe dot assemblies. Considering the fact that Cu(111) has much more pronounced surface states than Cu(100), Fig. 4 gives a strong indication that the substrate-mediated indirect coupling is likely associated with the presence of surfaces states. More theoretical study is clearly needed to understand the role of surface states on magnetic interactions.

Because of the random spatial distribution of the Fe dots, the indirect exchange interaction should induce some degree of spin frustration in the dot assembly. The degree of the spin frustration increases with increasing density and is reflected by the ratio of the remanent to saturation magnetization (M_r/M_s). Evidence of spin frustration in this system is shown in Fig. 3, as the M_r of the high-density dot assembly is less than a factor of 2 higher than that of the low-density assembly, despite the fact that its M_s value is 5 times higher. The power law fitting of the measured M vs T data that is shown in Fig. 3 yields distinctly different critical exponents (β) for the two assemblies. In magnetic phase transition, a decreased critical exponent is often interpreted to result from a decrease in the dimensionality of a magnetic system [18]. The change that we observe, however, may not directly link to the critical behavior of a phase transition due to the spin frustration.

In summary, we have observed an unusual ferromagnetic stability in Fe dot assemblies prepared with the aid of a Xe buffer layer on the Cu(111) surface. By growing assemblies of magnetic dots which have a fixed average size and varied spacing and then monitoring the resulting influence on the magnetic behavior, we were able to rule out enhanced anisotropy and dipolar interactions as the main contributors to the magnetic order. The strong dependence of the T_c values of Fe dots on the types of substrates suggests that the stable ferromagnetism is associated with an exchange interaction that is mediated by the substrate.

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