請包括前言、研究目的、文獻探討、研究方法、結果與討論（含結論與建議）…等。

精簡報告之篇幅以 4 至 10 頁為原則，完整報告之篇幅則不限制頁數。

附表及附圖可列在文中或參考文獻之後，各表、圖請說明內容。

若該計畫已有論文發表者，可作為成果報告內容或附錄，並請註明發表刊物名稱、卷期及出版日期。

參考文獻部份：若有與執行本計畫相關之著作、專利、技術報告、或學生畢業論文等，請在參考文獻內註明之，俾可供進一步查考。

計畫成果自評部份：請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

十二、研究計畫內容：

（二）研究計畫之背景及目的。請詳述本研究計畫之背景、目的、重要性及國內外有關本計畫之研究情況、重要參考文獻之評述等。本計畫如為整合型研究計畫之子計畫。

Magnetism is the heart of magnetic devices, especially the magnetic storage media that we use in our daily lives. There has also been progress in applying magnetism to computation, including qbits formed by spins in quantum dots[1] (Fig. 1 left) and classical bits by coupling small ferromagnetic islands[2] (Fig. 1 right).

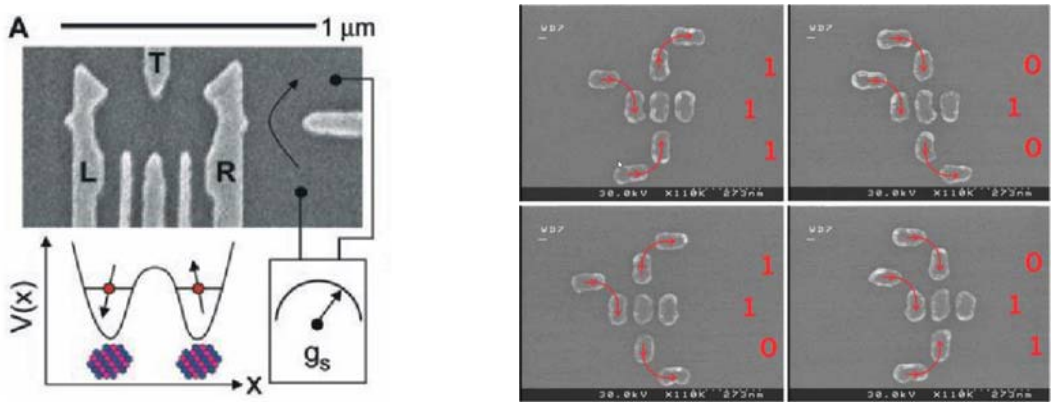

Figure 1: The left figure shows a double quantum dot acting as two coherent spin states. The system allows state preparation, coherent manipulation, and projective readout, and forms a long-lasting qubit. The right figure shows three magnets (red arrows), with the central one to be antiferromagnetic and the other two ferromagnetic, form logical gates according to their resulting magnetization directions due to a horizontal magnetic field.

Magnetism is also a topic that interests many physicists and chemists. Physicists can manipulate ferromagnetic islands on a surface (see Fig. 2) to form the so-called spin ice[3], a highly degenerate

magnetic ground state. In the mean time chemists can couple few atomic spins together in various structures, the well-known molecular magnets. The stereotypical molecular magnet is the Mn 4- acetate[4] (see Fig. 2). Molecular magnets are normally fabricated to have large net spins. In summary, there are two methodologies of making nanoscale magnets: the top-down approach (spin ice) where this method is very good for manipulating structures, but unfortunately it has not reached atomic-scale control. On the other hand if one uses the bottom-up approach like in chemistry, there is atomic-scale control, but the structure can not be easily manipulated after being built.

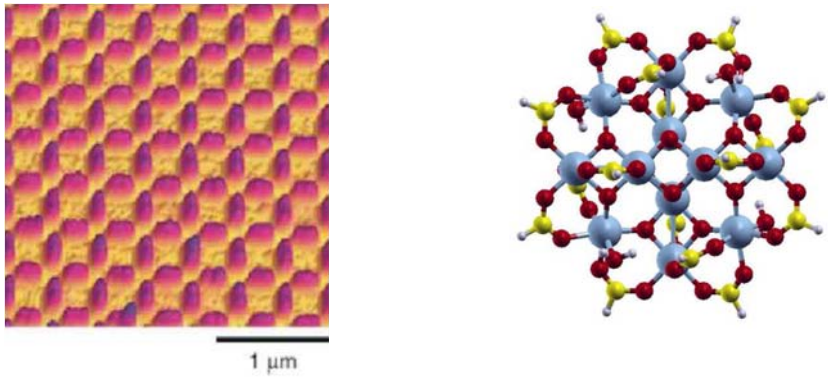

Figure 2: The left is a lithographically fabricated spin ice. The right is the ball-and-stick model of Mn12-ac, with methyl groups replaced for clarity by hydrogen atoms (large balls are Mn atoms).

There is a recent development by the low-temperature STM group at IBM Almaden Research Center that applies a technique somewhere in between the spin-ice and molecular-magnet approaches in making nanoscale magnets. This group has been pioneering in manipulating individual atoms on material surfaces. The earliest work was being able to spell out the letters I-B-M with individual Xe atoms in 1989, perhaps the most important landmark of nanoscience. The continuous works, Quantum Corral[5] and Quantum Mirage[6], have drawn so much attention of the scientific society.

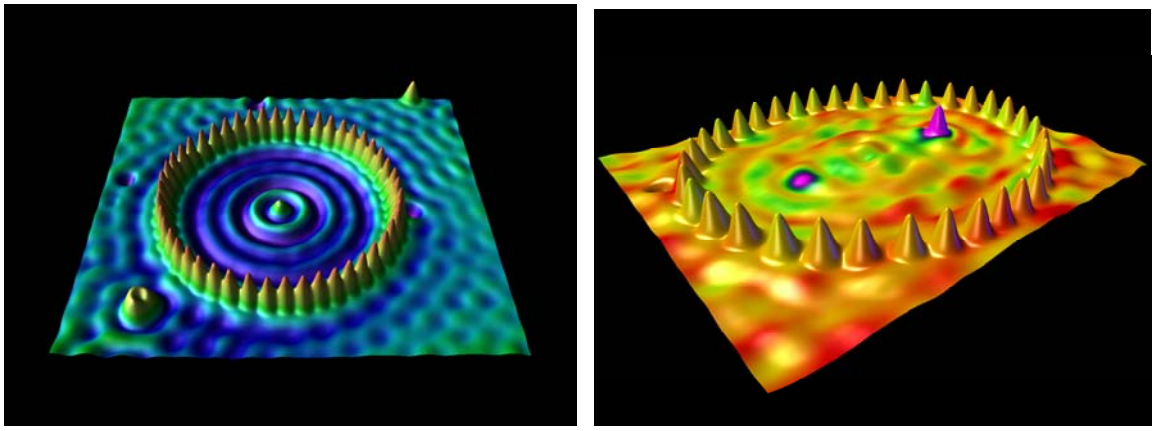

Figure 4: The left shows an STM image of direct observation of standing-wave patterns in the local density of states of the Cu(111) surface, called Quantum Corral. The circular corral of radius 71.3Å was constructed out of 48 Fe adatoms. The right shows that an elliptic corral projects the electronic states of the surface electrons surrounding the focal cobalt atom to the other focus of the ellipse that has no magnetic atom, called Quantum Mirage.

Their advance in atom manipulation on surfaces has recently made it possible to probe magnetism of individual atoms, as well as demonstrated that STM can build chains of Mn atoms and measure magnetic

excitation of such chains using Inelastic Tunneling Spectroscopy (IETS)[7]. This new technique can be used to explore the limits of magnetic data storage, by engineering the energy required to flip the collective orientation of a small number of magnetically coupled atoms.

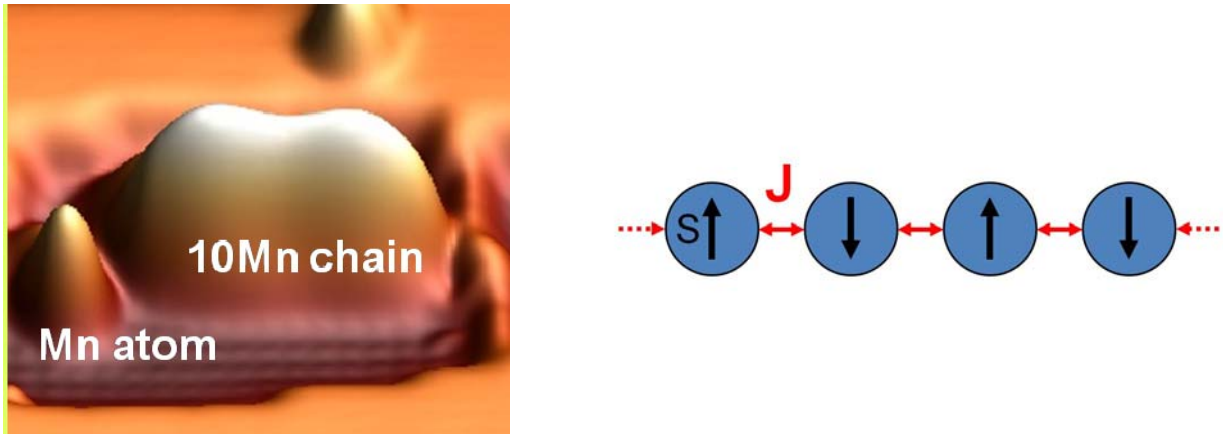

Figure 5: The left shows the perspective rendering of a chain of 10 Mn atoms. The right shows the schematic of the antiferromagnetically coupled atomic spins described by the Heisenberg model.

I have collaborated with the IBM Almaden STM group in probing the magnetic anisotropy of a single atom on a surface. This fundamental measurement has important technological consequences because it determines an atom's ability to store information. Previously, nobody had been able to measure the magnetic anisotropy of a single atom. This pioneering work on atomic-scale magnetic anisotropy was published at Science 317, 1199 (2007). With further work it may be possible to build structures consisting of small clusters of atoms, or even individual atoms that could reliably store magnetic information. Such a storage capability would enable nearly 30,000 feature length movies or the entire contents of YouTube – millions of videos estimated to be more than 1,000 trillion bits of data – to fit in a device the size of an iPod. Perhaps more importantly, the breakthrough could lead to new kinds of structures and devices that are so small they could be applied to entire new fields and disciplines beyond traditional computing. This work has drawn attention of the general public, and received news coverage widely. NBC TV news, August 30, 2007, "IBM is using this microscope to put atoms to work storing our data. These are building blocks to increase storage capacity by a factor of 1,000 ... then you would need 1,000 less times fewer energy saving energy and room all in a very small package as real as you might imagine." Wall Street Journal, "IBM and other companies are working to head off what may be an impending limit to hard-drive capacities. The company's technique might help break through that limit, by suggesting a way to store information in single atoms." Science Daily, "major progress in identifying a property called magnetic anisotropy, which determines an atom's ability to store information. That research, said IBM, could lead to storage of as many as 30,000 movies in a device the size of an iPod." Physics World, "Physicists at IBM have developed a technique that could allow data to be stored in bits containing as little as one magnetic atom."

（三）研究方法、進行步驟及執行進度。請列述：1.本計畫採用之研究方法與原因。2.遭遇之困難及解決途徑。3.重要儀器之配合使用情形。4.如為整合型研究計畫，請就以上各點分別說明與其他子計畫之相關性。5.如為須赴國外或大陸地區研究，請詳述其必要性以

及預期成果等。

This work is a pioneering work of computational study in STM engineered atomic spins. Previous study of the magnetic anisotropy of a single Fe spin has found an anisotropy energy of about 1meV, which gives rise to tolerance of thermal energy of order 0.1meV=1K. For device applications of less expensive cooling cost that works in liquid helium (boiling point 4K) or liquid Neon (boiling point 27K), tolerance of thermal energy is expected to be 1~3meV=10~30K, and requires anisotropy energy of 10~30meV. For device applications of reasonable cooling cost, tolerance of thermal energy is expected to be 10~30meV=100~300K (liquid nitrogen to room temperature), which requires anisotropy energy of 100~300meV. Further enhancement of the anisotropy energy will bring such a single anisotropic spin closer to the real application. The lathanoid atoms Tb and Dy are good candidates of obtaining larger anisotropy energy on the CuN surface because of their relatively large *L* and *S* compared to Fe. To calculate the Tb(Dy) atom on the CuN surface, we will first construct a CuN supercell of 5-layer slabs separated by 8 vacuum layers with the CuN monolayers on both sides of each slab and three Cu layers in between. To perform DFT-FLAPW[8] (Density Functional Theory with Full-potential Linearlized Augmented Plane Wave basis) calculation of a single Tb(Dy) atom on CuN, we will place Tb(Dy) atoms on top of the CuN surface at 10.80Å separation (same as the construction of Gd in Fig. 6).

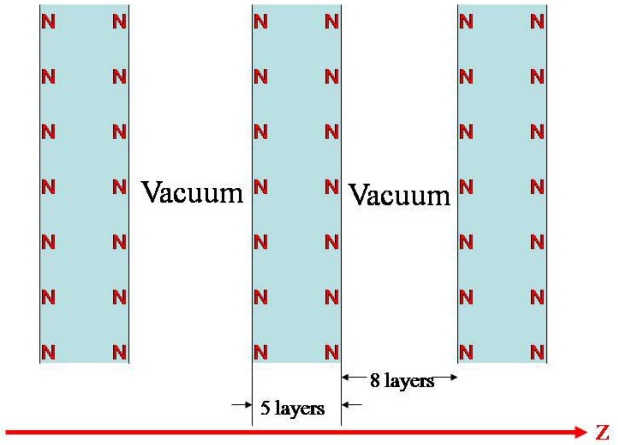

Figure 6: Periodic CuN slabs that simulate the CuN surface in my DFT calculation.

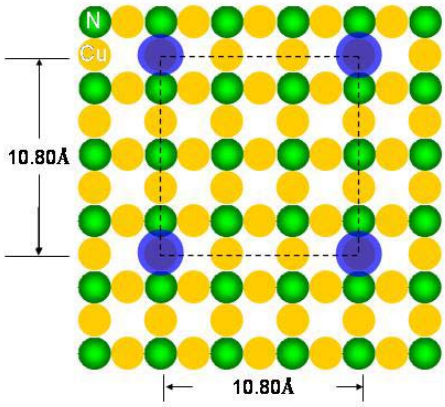

Figure 7: The top view of unit cells used to simulate a single Tb(Dy) atom (blue solid circles) on the CuN surface.

for a single Tb(Dy) atom on the CuN surface. The crystal structure is optimized until the maximum force among all the atoms reduces to 10 mRy/a_0. To understand the magnetic anisotropy, the first thing to do is to calculate the spin of Tb(Dy) on the surface although one expects to find a spin same as that of a free

atom based on the experiences learned from the previous studies. By using the PBE GGA exchange-correlation functional to perform DFT-FLAPW calculation of such systems, we obtain the following results

	Total magnetic moment in the simulated cell (unit: number of *e*)
Tb	0.0001
Dy	4.95

Table 1: Calculated magnetic moments of Tb and Dy when being placed on the CuN surface.

It is a bit surprised that Tb on the CuN surface has essentially no spin. Such an unexpected result requires a separate study and is beyond the scope of the current report. On the other hand, Dy on the CuN surface exhibits a magnetic moment consistent to an atomic configuration $4f^9$. A standard DFT-FLAPW calculation normally does not include the spin-orbit interaction. In such calculation the spin is not coupled to the lattice, and therefore it has no preferred direction. A system will exhibit magnetic anisotropy only when the spin-orbit interaction is considered. The classical explanation of spin-orbit coupling is that an electron moving with velocity $\boldsymbol{v} = \mathbf{p}/m$ in an external electric field $\mathbf{E} = -\nabla V(\mathbf{r})$ experiences a magnetic field given by the relativistic correction $\mathbf{p}/m \times (-\nabla V)/c$. Given a spherically symmetric potential $V(r)$ and accounting for the fact that the electron is spin-1/2, the interaction energy is then given by

$$H_{\mathrm{SO}} = \frac{e}{2m^2c^2r}\frac{dV}{dr}\mathbf{L}\cdot\mathbf{s}$$

The above equation is exact for spherical systems. In the FLAPW method the spin-orbit interaction is considered only within the muffin tin spheres, and the nonspherical potential is neglected when calculating dV/dr. The spin orientation is prescribed for a given DFT-FLAPW calculation, which gives rise to the total energy of the system of this particular spin orientation. By running calculations with the spin in the high-symmetry directions (in this project are *x*, *y*, *z* due to cubic symmetry), we have obtained the following energy differences among the symmetry axes for Dy on the CuN surface.

	Energy differences (meV)
$E_y - E_x$	37
$E_z - E_y$	36

Table 2: Calculated energy differences by pointing Dy spin differently. *x*, *y*, and *z*, stand for vacant-row, N-row, and out-of-surface directions. Lower energy means more prefered (stable).

This raises the magnetic anisotropy energy one order of magnitude in comparison with that of an Fe on the same surface (order of 1meV). The Fe magnetic anisotropy energy corresponds to an operating temperature of ~1K. Then Dy on the CuN surface corresponds to an operating temperature of 10~30K, doable in liquid helium (boiling point 4K) or liquid Neon (boiling point 27K). We are working with the IBM Almaden STM group to build such a system in the lab.

Our DFT calculations also find that most of the spin density is localized on the Dy atom and its surrounding interstitial region, with an accumulated magnetic moment of 4.70, corresponding to S=2.35. However, a substantial amount of spin density extends into the surrounding atoms, as illustrated in Fig. 8, where we find that the spin spreading occurs primarily to the nearest four Cu atoms at 45° between the N and the vacant directions in the surface molecular network. By including the spin of all of the atoms, the

net spin of the total structure is calculated to 2.475 (magnetic moment 4.95), very close to S=5/2. We also plot the density of states of Dy in the CuN surface. As one can see, the 4f spin-up states are all occupied, and 4f spin-down are partially filled, consistent with S=5/2. On the other hand, the 5d states are totally empty. Using the facts that S=5/2, and 5d band is empty, we conclude an atomic configuration $4f^9$ for Dy on this surface. We also compare the shape anisotropy of the spin density between Dy and Fe as show in Fig. 8. The Dy isosurface protrudes into the vacant direction, and the spin density spreading occurs primarily along the N direction. The two kinds of spin-density shape anisotropy compete with each other in producing their resultant magnetic anisotropy. As known from the spin-orbit calculation in Table 2, the vacant direction is the easy axis. This study demonstrates that the self shape anisotropy of a magnetic atom seems to produce larger magnetic anisotropy compared with its spin-spreading shape anisotropy.

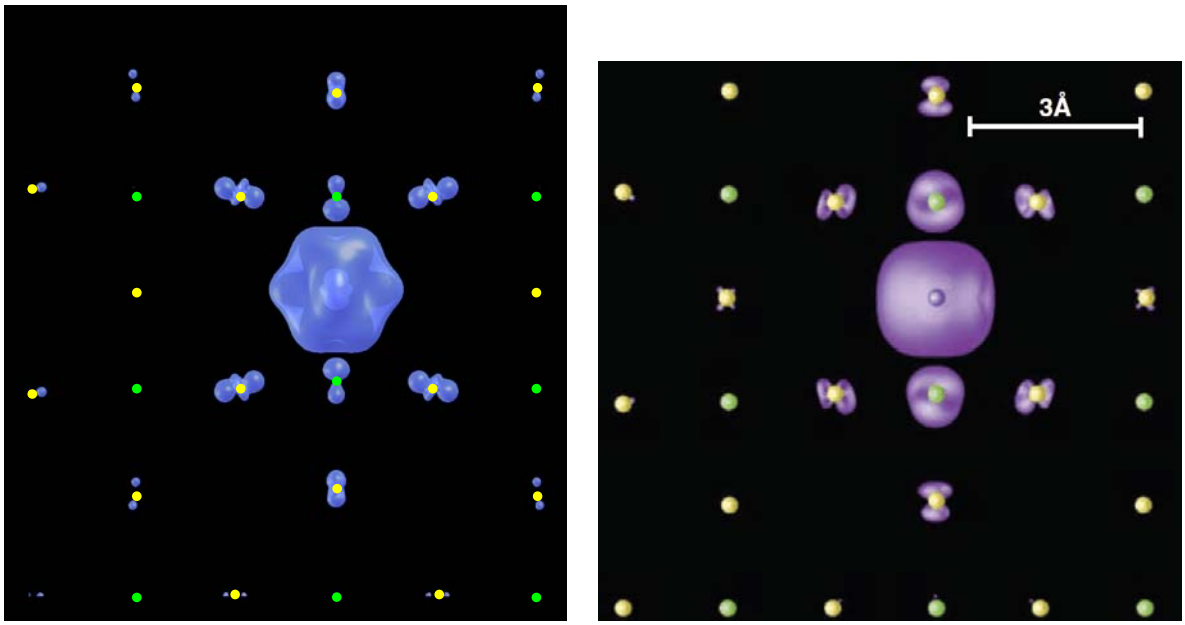

Figure 9: Calculated net-spin-density distribution for Dy (left) and Fe (right) on CuN. Contours (blue for Dy, purple for Fe) of constant net spin density (0.004 for Dy and 0.01 for Fe e/a_0), as calculated by DFT for an Fe atom adsorbed on a Cu site on a CuN surface. Only the Dy atom and the atoms in the CuN surface layer are shown for clarity.

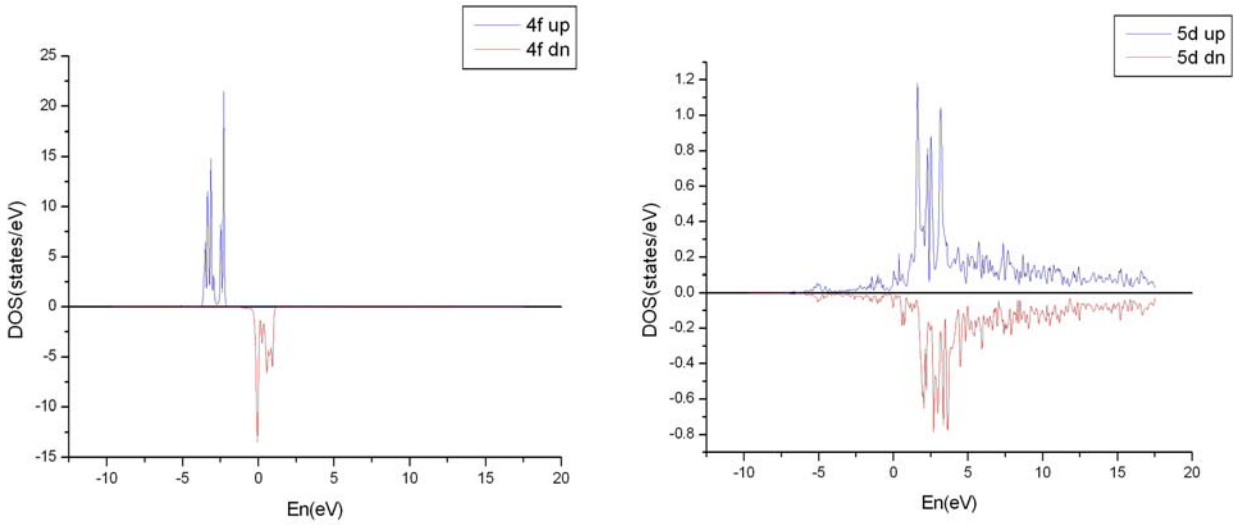

Figure 8: Projected densiy of states of a Dy atom when being placed on the CuN surface. Negative DOS refers spin down.

（四）完成之工作項目及成果。請列述：1.完成之工作項目。2.對於學術研究、國家發展及其他應用方面預期之貢獻。3.對於參與之工作人員，預期可獲之訓練。4.本計畫如為整合型研究計畫之子計畫，請就以上各點分別說明與其他子計畫之相關性。

The electronic structure of both a single Tb and Dy atom on the CuN/Cu(100) surface are calculated using DFT-FLAPW. The structure relaxation under the Tb (Dy) absorption is determined by minimizing the atomic forces. The calculated spin density is plotted in the three-dimensional space. The spin-density shape anisotropy of Dy shows that the *f* orbital can produce self shape anisotropy in addition to the spin spreading shape anisotropy. The relation between the spin-density shape anisotropy and the spin-anisotropy energy has also been studied. As the previous study of Fe has indicated, the most anisotropic direction of the spin density coincides the one of the spin-anisotropy easy axis. When this property is examined again for the Dy atom, we additionally find that the self shape anisotropy of a magnetic atom seems to produce larger magnetic anisotropy compared with its spin-spreading shape anisotropy. The total energies of the Dy atom on the the CuN surface were calculated, with the spin-orbit coupling included, by pointing its spin along the three directions: the out-of-surface *z*, the N-row *y*, vacant-row *x*. The calculated anisotropy energy is one-order-of-magnitude larger than that of Fe, leading to a less expensive operating temperature 10~30K (was 0.5~1K in the past) for spin orientation flip. Further improvement can eventually lead to information storage technology using the flip of individual atomic spins that are built one atom at a time by STM.

The students who participate in this project have learned how to perform first-principles calculation of material surfaces, including establishing the crystal structure of a given crystal surface, running the electronic-structure self-consistent cycle, and optimizing the crystal structure. The students have gained knowledge on the magnetic anisotropy of individual atoms. They have also become familiar with the computing architecture of the IBM Almaden Blue Gene supercomputer.

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