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Theory of giant saturation magnetization in α'' -Fe₁₆N₂: role of partial localization in ferromagnetism of 3d transition metals

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Abstract. A new model is proposed for the ferromagnetism associated with partially localized electron states in the Fe₁₆N₂ system that explains its giant saturation magnetization. It is demonstrated that an unusual correlation effect is introduced within the Fe–N octahedral cluster region and the effective on-site 3d–3d Coulomb interaction increases due to a substantial 3d electron charge density difference between the cluster and its surroundings, which leads to a partially localized electron configuration with a long-range ferromagnetic order. The first-principles calculation based on the LDA + *U* method shows that giant saturation magnetization can be achieved at sufficiently large Hubbard *U* values. The feature of the coexistence of the localized and itinerant electron states plays a key role in the formation of giant saturation magnetization.

The search for material with higher saturation magnetization becomes more crucial for high magnetic-energy-product permanent magnets and extremely high areal density magnetic recordings. It is well known that the greatest saturation magnetization value that has been achieved so far is $M_s = 2.45$ T with Fe₆₅Co₃₅ alloy [1]. Decades ago, it was claimed that one of

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the iron nitrides α'' -Fe₁₆N₂ possesses giant saturation magnetization far beyond the iron–cobalt alloy system, although currently this claim is still under scrutiny [2].

The α'' -Fe₁₆N₂ phase was discovered by K H Jack in the 1950s, which was reported as a metastable phase formed from a rapid quenching process from γ' -N-austenite [3]. Interest in its magnetic properties originates from a discovery by Kim and Takahashi in 1972 [4], when they reported giant saturation magnetization ($M_s = 2.58$ T) observed on Fe–N films synthesized by a thermal evaporation process. Almost 20 years later, research on this topic was stimulated by Sugita *et al* [5] based on the single-crystal α'' -Fe₁₆N₂ samples grown epitaxially on GaAs or In-doped GaAs substrates by molecular beam evaporation (MBE). The saturation magnetization was found to be 3.2 T for these samples, with a corresponding magnetic moment as high as $3.5\mu_B/\text{Fe}$ at low temperature. However, subsequent investigations by many other groups on bulk and thin films containing α'' -Fe₁₆N₂ led to conflicting results, with M_s less than 2.3 T ($2.5\mu_B/\text{Fe}$) [6, 7]. Somewhat higher moments have been reported in films prepared by specially designed deposition systems [8, 9], reaching values up to $2.9\mu_B/\text{Fe}$ – $3.0\mu_B/\text{Fe}$. However, none of these results has been repeated. Due to such inconsistent and poorly reproducible reports, Fe₁₆N₂ has been regarded as a mystery among magnetic researchers.

A general understanding of magnetism in iron nitrides is based on itinerant ferromagnetism. When nitrogen is accommodated in the iron octahedral clusters (voids) to form interstitial compounds, the 3d down-spin electrons redistribute themselves on different iron sites due to p–d hybridization between the N site and its nearest six iron neighbors [10]. Measurements on most iron nitride phases suggest quantitative agreement with this picture. However, in the case of α'' -Fe₁₆N₂, calculations based on local spin density approximation (LSDA) fail to predict magnetic moments as high as claimed by experiments, even when first-principles methods [11] or non-local correction have been considered [12].

To rationalize the high moment reports, Lai *et al* [13] postulated the existence of a strong correlation effect on all iron sites in the Fe₁₆N₂ system and obtained the magnetic moment more closely resembling the high moment experimental data. However, it has been argued whether the material system can maintain its metallic properties given the high on-site Coulomb U values and its inability to guide the experiment. Sakuma proposed a high moment scenario called the charge transfer model [14], inferring the existence of empty nitrogen orbitals near the Fermi level, which serve as charge hopping sites. This qualitative model predicts a high spin configuration of Fe and long-range ferromagnetic order through an effective ‘double exchange’ process in the context of a highly localized spin interacting picture. However, there is no clear evidence showing that the N site is much more negatively charged than the other sites in the iron nitrides. Recently, our group has performed x-ray magnetic circular dichroism (XMCD) measurements on high saturation magnetization Fe₁₆N₂ samples and discovered localized 3d electron states [15], which provide clear physics insight for the first time and experimentally confirm that the α'' -Fe₁₆N₂ system has a dual electron configuration. This observation implies that neither itinerant nor localized magnetism alone can fully describe the mechanism in the Fe₁₆N₂ system. In this paper, a new model is provided to address this longstanding giant saturation magnetization problem based on the idea of 3d electron partial localization. It is shown that there is a considerable charge density difference inside and outside the Fe–N octahedral clusters due to reduced symmetry in the Fe₁₆N₂ system. As a result, the electron correlations inside and outside the cluster region possess different natures. LSDA with on-site Coulomb (U) correction (LDA + U)-based calculation is performed to illustrate the essential

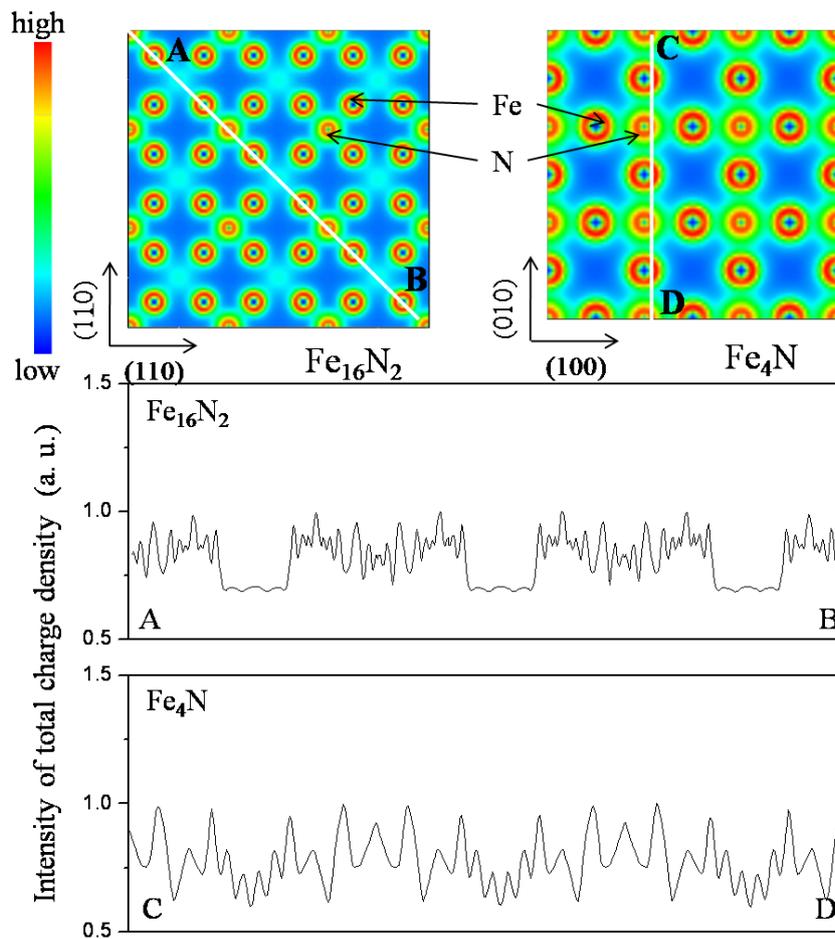


Figure 1. Total charge density distribution projected on the Fe–N plane perpendicular to the [001] plane for Fe_{16}N_2 and Fe_4N based on LDA calculation results. The lower figures show intensity of charge density (logarithmic scale and normalized to their maximum intensities) along lines AB and CD as marked in the charge density figures, shown to illustrate the effect of broken symmetry as explained in the text.

features of the physical picture discussed here. As expected, giant saturation magnetization can be realized for sufficiently large U values.

The crystal structure of Fe_{16}N_2 contains Fe with the local environment similar to both bct-Fe (with $c/a \sim 1.1$) and fcc-Fe (Fe_4N). In both bct-Fe and fcc Fe_4N , a D_{4h} symmetry Fe is formed due to lattice expansion along the [001] direction. However, in a real Fe_{16}N_2 system, the Fe sites with local D_{4h} point group symmetry reduce to C_{4v} and C_{1h} symmetry due to the alternating occupancy of the N atoms. Unlike Fe_4N or bct-Fe, the corner Fe sites within those distorted Fe–N octahedral clusters lose the mirror reflection symmetry along certain directions, experiencing a less symmetric crystal field due to the central N. Therefore, an additional effect arises due to the symmetry break. Figure 1 plots the total charge density for Fe_4N and Fe_{16}N_2 on the Fe–N plane perpendicular to the [001] direction based on the LDA method. As illustrated in the figure, in Fe_4N , Fe–N octahedral clusters are connected through the corner Fe, which results in a relatively uniform charge distribution along line CD. On the contrary, in Fe_{16}N_2 ,

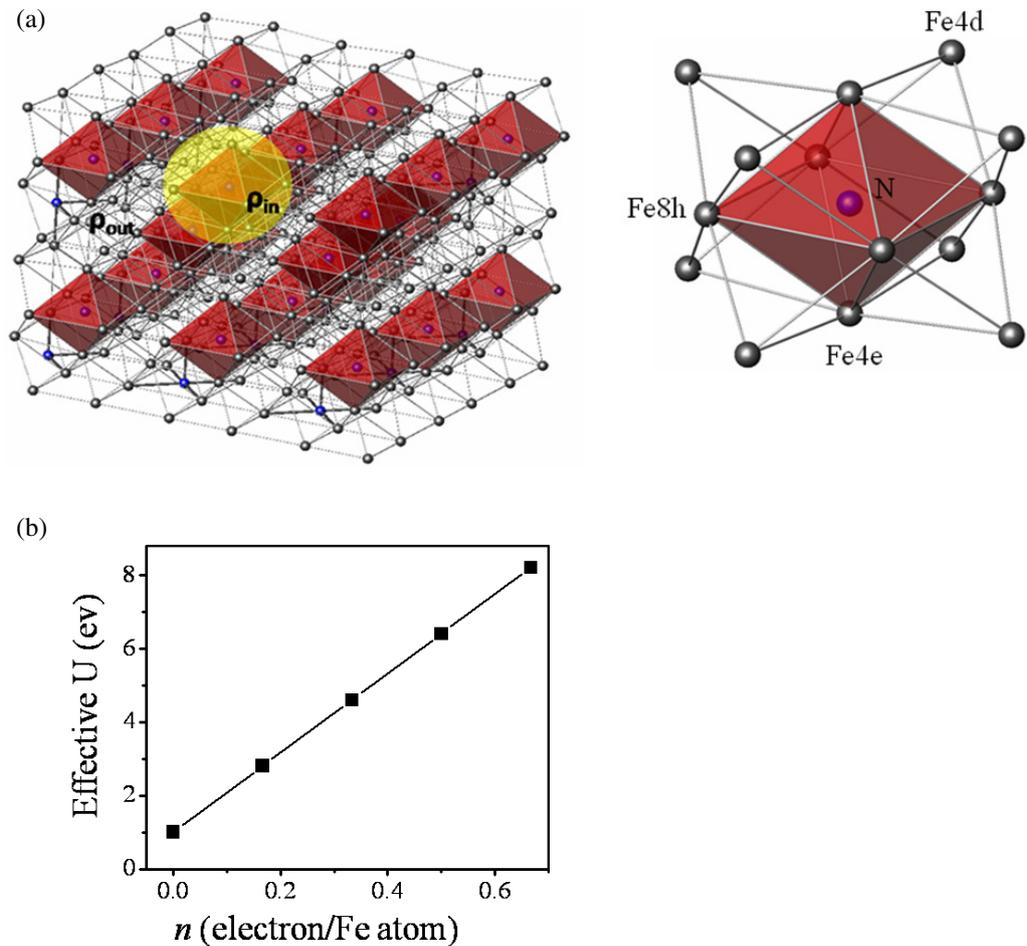


Figure 2. (a) Crystal structure of Fe_{16}N_2 . Fe–N octahedral clusters are highlighted in red. The proposed charge density distribution is schematically drawn with a yellow sphere. ρ_{in} and ρ_{out} as marked in the figure illustrate such difference. The right figure shows the chemical environment of the three iron sites: Fe8h and Fe4e are within the cluster region and Fe4d is outside the cluster. (b) 3d electron charge difference per iron site between the interior and exterior of the Fe–N octahedral cluster versus the effective on-site Coulomb U .

Fe–N octahedral clusters are geometrically isolated in the sense that each corner Fe site belongs to an individual Fe–N octahedral cluster. As a result, there appears a significant charge density difference inside and outside the Fe–N octahedral cluster region, which originates from this reduced symmetry. These observations lead us to suggest the 3d electron partial localization model for the strong ferromagnetism in this Fe_{16}N_2 material system.

The starting point for a discussion of the partial localization model is that there exists a considerable 3d electron charge density difference between iron sites inside and outside the Fe–N octahedral cluster. To illustrate the charge density effect on its magnetic properties, a model calculation is performed to capture the essential qualitative features. Considering a uniform and spherical d electron charge distribution within the Fe–N octahedral cluster, as illustrated schematically in figure 2(a), the static potential difference between the interior and exterior of the clusters can be obtained by solving Poisson's equation. This potential can be

written as $\frac{2\pi}{3}(\rho_{\text{in}} - \rho_{\text{out}})a_0r_0^2$ Ryd, where ρ_{in} and ρ_{out} represent the d electron charge density inside and outside the sphere, respectively, a_0 is the Bohr radius and Ryd is the Rydberg constant. This potential energy difference is created solely by the short-region repulsive electron interaction as a screened Coulomb energy in electron gases, which qualifies an on-site Coulomb interaction difference between the Fe–N octahedral cluster and its metallic environment (Fe4d). The U values found in metallic Fe are typically 1 eV [16]. Figure 2(b) plots the effective U value within the cluster versus n , which is defined as the average number of 3d electrons per Fe inside the Fe–N octahedral cluster minus those outside the cluster. According to our model, n increases linearly as U increases, reaching a value of $n \sim 0.5$ at U around 7–8 eV. In the LSDA picture, the number of 3d electrons per Fe on Fe4d, Fe4e and Fe8h sites calculated by He *et al* [17] is 6.65, 6.57 and 6.58, respectively. In our model, if ~ 0.4 3d electrons transfer from the Fe4d site to its four neighboring Fe–N octahedral clusters, the number of 3d electrons per Fe for Fe4d, Fe4e and Fe8h is 6.25, 6.70 and 6.71, respectively, and $n \sim 0.5$ can easily be reached. At this point, the physical picture is rather clear. Some amount of 3d electrons transfer from the Fe4d site to the Fe–N octahedral cluster and give rise to local potential energy fluctuations, which result in a large U difference between the Fe–N octahedral cluster and its surrounding iron atoms. To stabilize this charge transfer process, an additional energy term is required to compensate the U increase. Therefore, the bonding between Fe and N plays an important role. In analogy to Stoner’s ferromagnetism stability argument, a high U value leads to the reduction of band overlapping between spin up and spin down, and it effectively increases the exchange energy. Ultimately, certain orbitals within the Fe–N octahedral cluster will possess localized structure with fully polarized spin configuration, where Hund’s coupling dominates. On the other hand, the other orbitals remain with broad bandwidth and less exchange splitting due to their spatial extension and strong hybridization with neighboring metallic Fe4d sites outside the Fe–N octahedral cluster. This condition helps maintain their band-like features that favor long-range ferromagnetic coupling and metallic behavior. In that sense, dual electron behavior and partial localization are realized.

To further illustrate this idea quantitatively, an electronic structure calculation with on-site Coulomb interaction corrections was performed to compute the magnetic moment in Fe_{16}N_2 . To simulate partial localization, we used the LDA + U method used by Anisimov *et al* [18]. The U value of Fe outside (Fe4d) the cluster sphere was fixed at 1 eV and the magnetic moment change was then plotted for three Fe sites as the U inside the cluster (the same U was assumed for both Fe4e and Fe8h) varied, as shown in figure 3(a). The J parameter (Stoner parameter) was taken to be $U/10$. Calculation was performed by using the Vienna *ab initio* simulation package (VASP), with projector augmented wave potential [19]. A plane wave cutoff corresponding to a kinetic energy of 250 eV was used. A k mesh of $8 \times 8 \times 8$ was used to sample the supercell. The exchange correlation function was approximated with the fully localized limit of the LSDA + U method [20]. The lattice constant was constrained according to its bulk value. The density of states (DOS) was calculated with fine k meshes using a tetrahedron method with Blöchl corrections as implemented in VASP. Both Fe4e and Fe8h sites sit inside the Fe–N octahedral cluster. As U increases, these sites favor rapid polarization, whereas the Fe4d site, which sits outside the Fe–N cluster, exhibits a slow decay of the moment from 2.9 to $2.6\mu_{\text{B}}/\text{Fe}$ and levels off at high U values. It is seen that when U is large enough, an average magnetic moment above $3\mu_{\text{B}}/\text{Fe}$ is obtained. It is important to discuss the choice of $U = 1$ eV for the Fe4d sites. A recent study shows that a U close to 2–3 eV is considered in metallic Fe [21]. According to our calculation, when $U = 1$ eV is applied to all three iron sites, the magnetic moments calculated

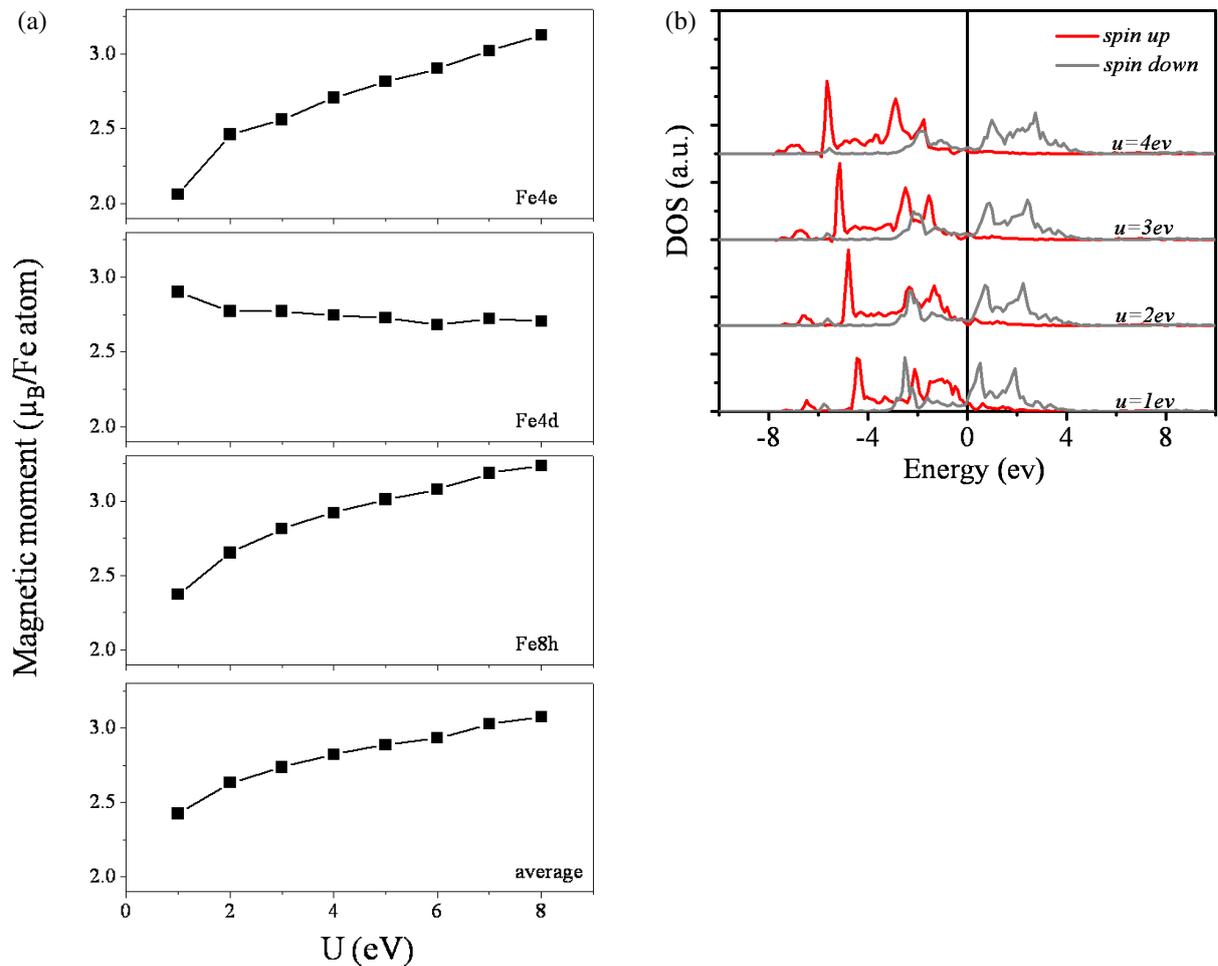


Figure 3. (a) Local magnetic moment of three different Fe sites (Fe4d, Fe4e and Fe8h) in Fe_{16}N_2 versus Coulomb U change. Magnetic moment of different Fe sites in Fe_{16}N_2 versus U as explained in the text. (b) Partial DOS projected on $(dxz + dyz)$ of the Fe4e site in Fe_{16}N_2 for different U values.

coincide with those derived from the standard LSDA calculation. This result implies that a U value around 1 eV should be sufficiently small to give rise to the results based on the traditional calculation. It is possible that U can be less than 1 eV for the Fe4d site without jeopardizing its itinerant electron feature. In that case, a reduced average magnetic moment should be expected, although the monotonic trend of the magnetic moment versus U still remains. The U values considered in the Fe4e and Fe8h sites are up to 8 eV. In reality, $U \sim 6$ eV is used for insulator FeO [18], in which the screening effect is expected to be weaker than that in Fe_{16}N_2 . Therefore, although no first-principles calculation on the U value can be retrieved, a reasonable estimation of the actual U value should be positioned in between metal Fe and FeO. In the model discussed here, at $U = 4$ eV, the average moment reaches a value of $\sim 2.8\mu_B/\text{Fe}$, which already exceeds the known limit for ferromagnetism ($\sim 2.6\mu_B/\text{Fe}$ in $\text{Fe}_{0.65}\text{Co}_{0.35}$).

The effect of d-d Coulomb interaction on electronic structure can be explained in the following. Figure 3(b) plots the partial DOS projected on double degenerate $(dxz + dyz)$ orbitals

of Fe4e sites. As U begins to increase, the spin-up band shifts downwards with more and more states occupied at the expense of the spin-down orbital in the process of self-consistency iteration. This orbital will eventually become fully occupied when U is sufficiently large. In that case, electrons on these orbitals exhibit nearly atomic configuration and the on-site magnetic coupling mechanism is dominated by Hund's rule, which gives rise to a high spin configuration of Fe. It is also interesting to note that the Fe4d sites reduce their magnetic moment as U increases. This suggests that the electron distribution on different iron sites changes significantly in comparison with the LSDA calculation results, in which case the high magnetic moments on the Fe4d sites are due to the charge transfer from Fe4d to the Fe sites closer to the N sites.

The essential difference between our model and those of others is the idea of 3d electron partial localization. The LDA + U methods were initially developed to treat Mott insulator systems, such as FeO. The earlier Lai model considers a strong correlation effect on all three iron sites and achieves high magnetic moment. The U values used are calculated from the embedded cluster method [22] by assuming a relatively small screening constant, which has been considered as 'unrealistic' for a metal system [23]. Experimentally, the low-temperature transport properties suggest the legitimacy of treating Fe₁₆N₂ as a metal [24]. However, a large residual resistivity is also explored relative to the pure metal Fe, implying the existence of defect-like localized electron states even though single-crystal samples are used for this study. Recently, our group has performed similar measurements that confirmed this observation [25]. In our model, we emphasize that the unusual correlation occurs within the Fe–N octahedral clusters due to the introduction of the central N atom. The metallic behavior of the system still stands as the U on the Fe4d sites remains metal-like. More importantly, the difference of the on-site Coulomb U for the three iron sites distinguishes the material into two subsets: Fe–N octahedral clusters (Fe8h and Fe4e) and metallic Fe atoms (Fe4d). Within the Fe–N octahedral clusters, Fe8h and Fe4e possess a partially localized electron behavior due to the enhancement on U . Outside the Fe–N octahedral clusters, Fe4d maintains its metal-like behavior. The macroscopic giant ferromagnetic order is formed through the interplay between localized orbitals and the itinerant band. Therefore, to rationalize the giant saturation magnetization report, dual electron behavior seems to be a necessity at a fundamental level. This opens up the possibility of identifying promising candidates for many applications that demand high M_s .

In conclusion, we proposed for the first time an insight physics/model that some Fe atoms in Fe₁₆N₂ are more influenced by Coulomb repulsion (Hubbard U) than others. This scenario is consistent with Fe₁₆N₂'s unique crystal structure, which consists of the chemically ordered octahedral Fe6–N cluster +Fe atoms. Careful calculations using the LDA + U method gave a theoretical justification for the possible giant magnetism observed in Fe₁₆N₂. With a reasonable choice of Hubbard U value (3–4 eV), an average magnetic moment of $2.8\mu_B/\text{Fe}$ was obtained, which exceeds that of Fe₆₅Co₃₅ alloy. The partial localization concept provides an insight into the effect brought about by N sites. In particular, isolated Fe6–N octahedral clusters induce non-uniform charge distribution and cause an increase in the effective U value that creates both localized and itinerant 3d electrons. This feature allows the system to have global ferromagnetic coupling while locally maintaining Hund's rule dominated magnetic moments. The model proposed here examines the magnetism in Fe₁₆N₂, which is presumably viewed as a non-conventional ferromagnetic metallic system. For Fe atoms in metal, a pure band theory description is not capable of yielding such large moments given the fact that spin exchange and correlation included in the standard LSDA approach are usually underestimated. Therefore, a parameterized many-body approach (LDA + U) was explicitly applied, since in the completely

localized electron scheme the high local moment correlates well with the prediction based on Hund's rule. We believe that in this proposed scenario, clusters (providers of local electrons) + atoms (providers of itinerant electrons) can be applied to understand and design other material systems, and other new physical properties could be expected too. However, we also realize that further experiments are needed urgently to find direct evidence of the charge transfer from outside Fe atoms to Fe atoms of the Fe₆-N octahedral cluster. This work also highlights an urgent need to calculate the U values for Fe₁₆N₂ based on a real first-principles calculation.

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