

Spin-density distribution in ferromagnetic α'' -Fe₁₆N₂

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(Received 9 August 1994)

The electronic structure and the spin-density distribution in α'' -Fe₁₆N₂ crystal are calculated using the first-principles orthogonalized linear combinations of atomic orbitals method in the local-spin-density approximation. We found no evidence for a giant magnetic moment in this crystal although the Fe(III) site has a large moment of about $2.9\mu_B$. This result contradicts earlier experimental data, but is in close agreement with recent measurements.

There has been continued controversy regarding the existence of a giant magnetic moment in the intermetallic Fe compound, α'' -Fe₁₆N₂.¹ Since the early report of Kim and Takahashi more than 20 years ago,² many experimental reports³⁻⁶ indicate that this phase has a magnetic moment far above the pure Fe, α -Fe. More recent measurements seem to dispute this claim.⁷⁻⁹ On the other hand, theoretical calculations⁹⁻¹⁴ show the average moment in α'' -Fe₁₆N₂ is only slightly larger than that of Fe, far below that is needed to reconcile with the earlier experimental data. There are several potential explanations for this controversy: (1) Since pure single-crystal α'' -Fe₁₆N₂ is not easy to synthesize, there could be other hidden impurity phases in the thin-film samples with real large magnetic moment yet to be identified. (2) The experimental values deduced from various types of magnetic measurements are not precise because of the need for many intricate corrections. (3) Surface and interface effects may play a role since it is known magnetic atoms on the surface usually have their moments enhanced.¹⁵ (4) The local-spin-density approximation (LSDA) used in almost all theoretical calculations is inadequate for the α'' -Fe₁₆N₂ system.

In this paper, we would like to add further insight into this problem by presenting the detailed spin-density calculation in the α'' -Fe₁₆N₂ crystal using a state-of-the-art method. Although several calculations on α'' -Fe₁₆N₂ already exist, most of the calculation used the linearized muffin-tin orbital method in the atomic-sphere approximation (LMTO-ASA) or the augmented spherical wave method which are known to have results somewhat dependent on the choice of atomic-sphere radius. Even when the same atomic radii were used, different researchers using the same method tend to give different results.¹⁰⁻¹² The full-potential linearized augmented plane-wave (LAPW) calculation of Coehoorn, Daalderop, and Jasen¹³ seems to give the most reliable result so far. Results from another independent method is therefore very valuable. We use the spin-polarized version of the self-consistent orthogonalized linear combination of the atomic orbitals method (OLCAO) within the LSDA scheme. This is a very accurate all-electron method in which the basis functions are expanded in terms of atomic orbitals consisting of Gaussians. All interaction in-

tegrals are evaluated in real space. Unlike the LMTO method, the OLCAO method has no atomic-sphere radii associated either with the basis function or the potential function, and hence is more reliable to obtain the site-decomposed moments on various Fe sites and on N. It has been shown that nitrification of Y₂Fe₁₇ can lead to very complicated nonspherical spin-density distribution and diminished moments on the Fe atoms next to N.¹⁶ The real-space description of the wave function enables us to present detailed charge and spin-density distributions in this crystal, thereby providing further insight on the charge transfer and chemical bonding effect in relation to its magnetic properties. We refer the details of the method to the published literature.¹⁷

Figure 1 shows the crystal structure of α'' -Fe₁₆N₂ as determined by Jack in the early 1950's.¹⁸ There are three Fe sites, (4e), (8h), and (4d), respectively, labeled as Fe(I), Fe(II), and Fe(III). N sits at the center of the octahedron formed by four Fe(II) atoms in the x - y plane and two Fe(I) atoms above and below. The interatomic distances are listed in Table I. Figure 2 shows the calculated valence electron density on three different crystal planes, [100] plane containing Fe(I), Fe(III), and N atoms, [001] plane containing only Fe(II) and N; and the [110] plane which contain all the atoms. Figure 3 shows the spin-density distributions in color graphics on the same planes. Major observation of these maps can be summarized as follows: (1) The charge distributions around the Fe or the N atoms are rather spherically symmetric, but not the spin densities. (2) There is some evidence that N atoms form partially covalent bonds with the neighboring Fe(I) and Fe(III) atoms. (3) N is negatively polarized, although the region of negative spin density around N is rather small. (4) The Fe(II) site is very spacious, resulting in larger regions for the charge and spin densities. (5) There is an average charge transfer of 0.56 electron from the neighboring Fe atoms, mostly from Fe(II) and Fe(III) to N.

The calculated site-decomposed moments are listed in Table II. Also listed are the results from other calculations⁹⁻¹⁴ and the recent experimental data.^{7,9} As can be seen, there are greater variations among various LMTO and ASA calculations.^{9-12,14} Our calculated moments are quite close to but are slightly larger than the LAPW

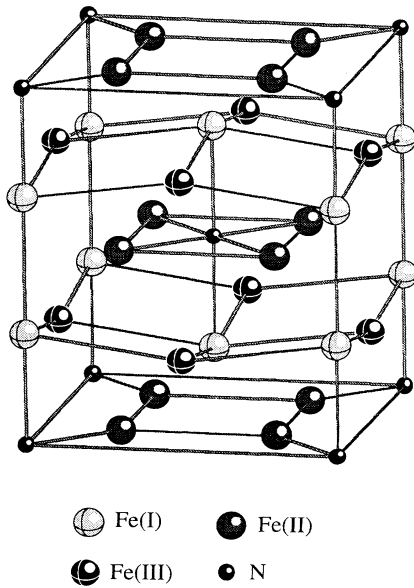


FIG. 1. Crystal structure of α'' - Fe_{16}N_2 .

calculation,¹³ and are in closer agreement with the recent experimental data of Coey *et al.*⁹ The Fe(III) site has a large moment of $2.90\mu_B$ basically because of its larger interatomic Fe-Fe separation. The average moment is $2.44\mu_B$ which is only 5% smaller than the measured average value of $2.57\mu_B$, and slightly larger than the LAPW value of $2.37\mu_B$. However, the average Fe moments from all these calculations are not much different. It is therefore unlikely for α'' - Fe_{16}N_2 with a structure as determined by Jack to have giant magnetic moment. The increase in moment for the Fe(III) site is not entirely due to an increased interatomic separation. From Table I, we see that the average nearest-neighbor Fe-Fe separations are 2.69, 2.62, and 2.67 Å for Fe(I), Fe(II), and Fe(III), respectively. There are all substantially larger than the Fe-Fe separation of 2.42 Å in α -Fe, yet the calculated moment for the Fe(I) site is only $2.06\mu_B$. In a model calculation for amorphous Fe,¹⁸ it was shown that the Fe moments can be smaller than 2.0 or larger than 3.0, depend-

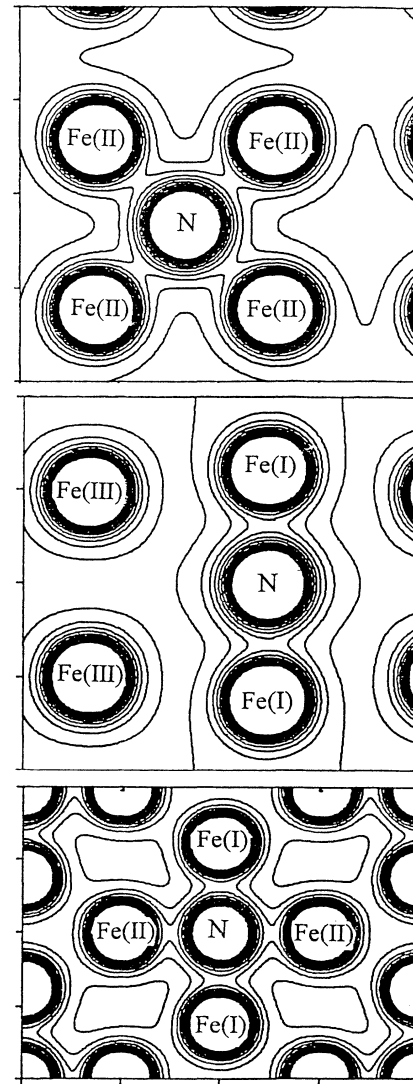


FIG. 2. Calculated charge density of α'' - Fe_{16}N_2 in (a) [001] plane, top panel; (b) [100] plane, middle panel; (c) [011] plane, bottom panel. The contour lines are from 0.02 to 0.22 in the unit of $0.02 [e/\text{a.u.}^3]$.

TABLE I. Near-neighbor atom numbers and interatomic distances in α'' - Fe_{16}N_2 .

		Fe-Fe separation (Å)	Average Fe-Fe separation (Å)
Fe(I):	with Fe(I):	2.390(1)	2.649
	with Fe(II):	2.349(2), 2.809(2)	
	with Fe(III):	2.885(4)	
	with N:	1.995(2)	
Fe(II):	with Fe(I):	2.349(2)	2.617
	with Fe(II):	2.860(4)	
	with Fe(III):	2.562(8)	
	with N:	2.022(4)	
Fe(III):	with Fe(I):	2.885(4)	2.670
	with Fe(II):	2.562(8)	

ing on the local short-range order determined by both the number of near neighbors as well as their separating distances.

The spin and site-polarized density of states (DOS) for $\alpha''\text{-Fe}_{16}\text{N}_2$ are shown in Fig. 4. The sharp peaks near -16 eV and -6 to -7 eV are from the N $2s$ and N $2p$ states. An important feature is that the Fermi level cuts at a very steep edge in the majority-spin band and at a minimum in the DOS of the minority-spin band. This

implies that the values of DOS at the Fermi level, $N(E_F)$ will be very sensitive to the Fermi energy. For that reason, we used a large number of k points to locate the Fermi level accurately. The calculated $N(E_F)$ values are 5.10 and 1.51 states/eV cell for the majority and the minority-spin bands, respectively, if we use the accurate analytic linear tetrahedron method. However, if a Gaussian broadening of only 0.05 eV (full width at half maximum) is applied, the $N(E_F)$ values change to 4.29 and 2.38 states/eV cell for the up and down spin bands, respectively.

It has been argued that a giant magnetic moment in $\alpha''\text{-Fe}_{16}\text{N}_2$ may exist. The failure of theoretical calcula-

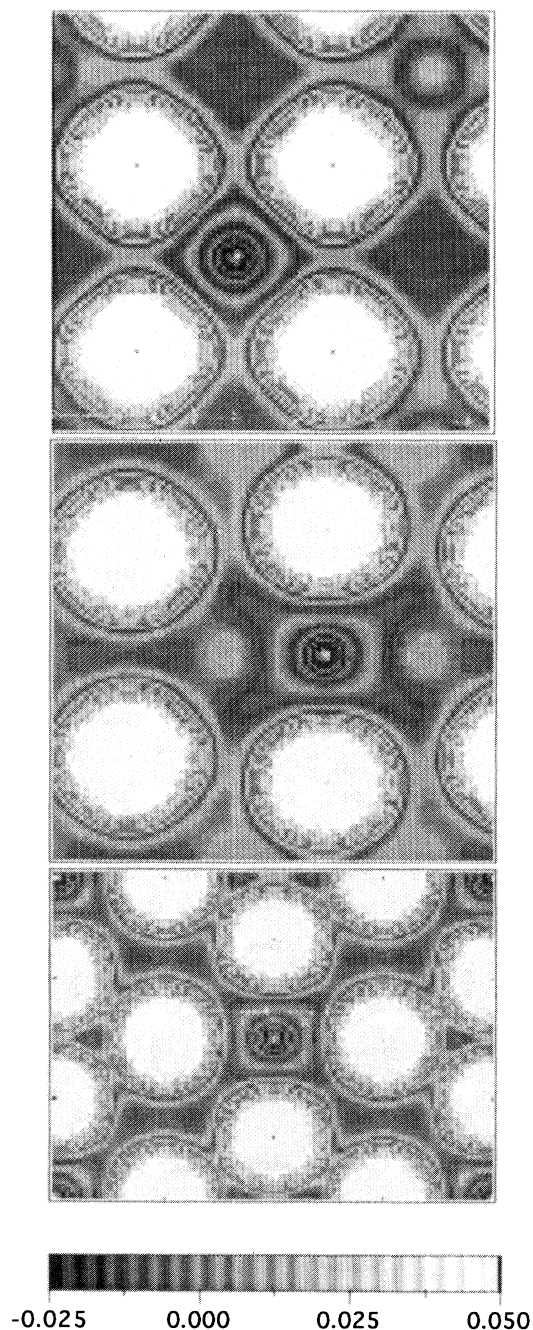


FIG. 3. Calculated spin density in the same planes as in Fig. 2. The scale is shown as color bar below.

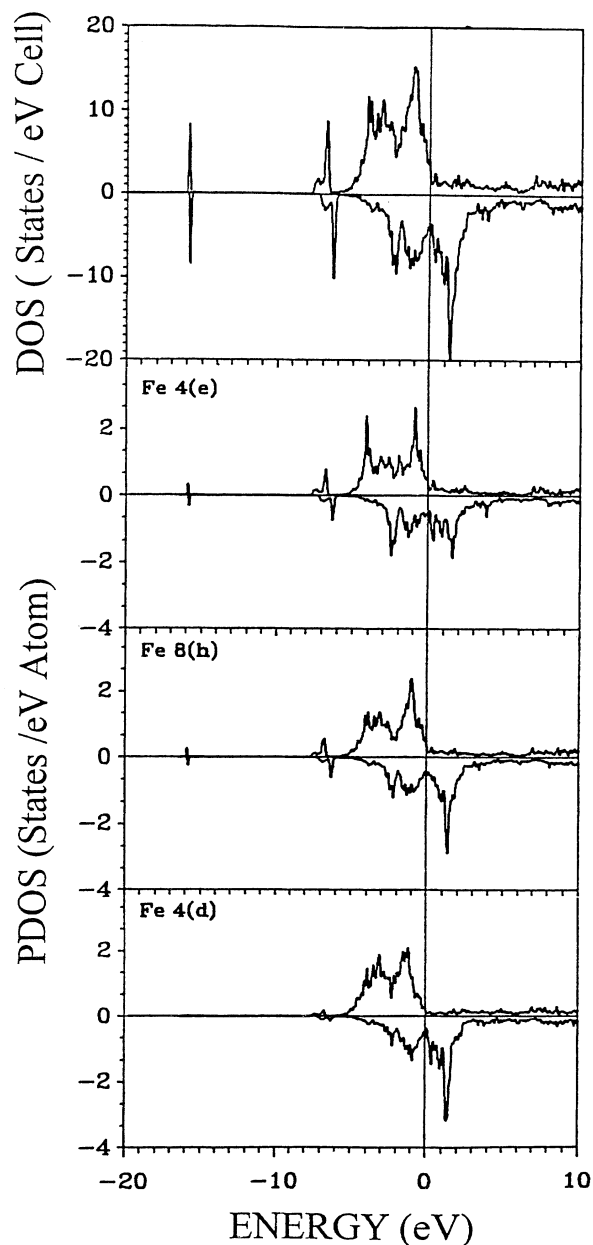


FIG. 4. Calculated spin-polarized total and partial DOS of $\alpha''\text{-Fe}_{16}\text{N}_2$: top panel, Total DOS. Others as indicated.

TABLE II. Calculated Fe moment (μ_B) and the $N(E_F)$ (states eV-spin-cell) in α'' -Fe₁₆N₂.

Site	This work	Sakuma ^a	Matar ^b	Min ^c	Lai ^d	Coehoorn ^e	Coey ^f	Expt. ^g	Expt. ^h
Fe(I)	2.06	2.27	2.30	2.15	2.00	2.04	2.21	2.33	1.5
Fe(II)	2.42	2.25	2.37	2.50	2.51	2.33	2.39	2.45	2.5
Fe(III)	2.90	2.83	2.89	2.85	2.98	2.82	2.81	3.05	3.8
N	-0.06	-0.07	-0.03	0.06		-0.01			
Average Fe	2.44	2.43	2.48	2.50	2.50		2.37	2.45	2.57
2.58									

^aReference 10.^bReference 11.^cReference 12.^dReference 14.^eReference 13.^fReference 9.^gReference 9.^hReference 7.

tion to produce a large moment can be attributed to the inadequacy of the LSDA theory. In our opinion, this is unlikely since LSDA theory works pretty well in other transition-metal intermetallic compounds and there is no compelling reason why it should fail in α'' -Fe₁₅N₂, or why correlation effect should be particularly important in this compound. Lai, Zheng, and Hu introduced an *ad hoc* Hubbard-like parameter "U" in the LSDA Hamiltonian and obtained an enlarged average moments of $2.85\mu_B$.¹⁴ Apart from several rather arbitrary parameters used in the calculation, their argument is not convincing enough since this scheme was originally suggested for Mott insulators,²⁰ a class of material known for its large correlation effects, but not for intermetallic compounds with a large bandwidth. If a similar calculation is carried out for, say, the rare-earth Fe compounds such as Nd₂Fe₁₄B, or Y₂Fe₁₂N₃ where experimental data are

much less controversial, and the magnetic moments obtained are close to the LDA result and the experiment, then the argument for strong correlation effect in α'' -Fe₁₆N₂ will be more convincing.

In conclusion, we have carried out a high-precision spin-polarized calculation for α'' -Fe₁₆N₂ using the spin-polarized OLCAO method. We obtained site-decomposed Fe moments in close agreement with the more recent data. Although the Fe(III) site appears to have a large moment, there is no evidence for giant moment in this crystal as suggested by the earlier experimental measurements. We found the N atom has a negative polarization and form a partially covalent bonds with the neighboring Fe(I) and Fe(II) atoms.

This work was supported by U.S. Department of Energy Grant No. DE-FG02-84ER45170.

¹See, for example, Session EB, *Fe₁₆N₂: Giant Moment or Not*, The 6th Joint MMM-Intermag Conference, June 20–23, Albuquerque, New Mexico.

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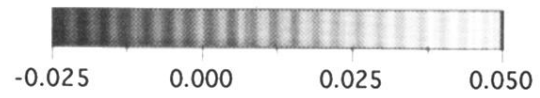
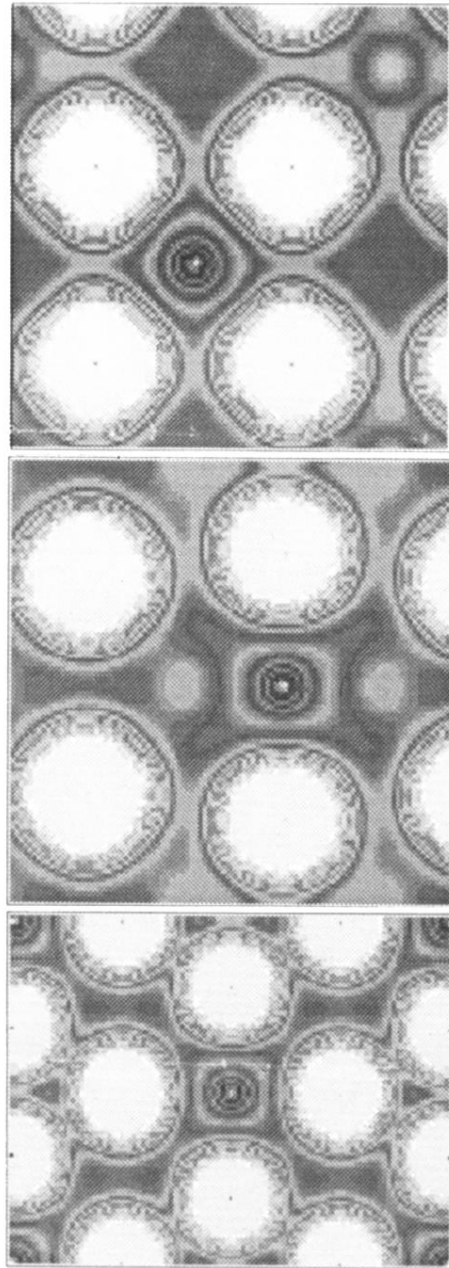


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