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Spin-polarized linear muffin-tin orbitals calculation of the interstitial-atom effect in γ'-Fe_4Z (Z=H, C, N)

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The spin-polarized linear muffin-tin orbitals method is applied to calculate the electronic structure of γ'-Fe_4Z (Z=H, C, N) and the γ'-Fe_4E which is γ'-Fe with an empty sphere insertion. The chemical bonding effects of the interstitial Z atom are substantially investigated. The results indicate that the insertion of the Z atom changes not only the Fe-Fe interaction, but also the Fe-Z interaction. The latter is observed to be depending on the chemical properties of the Z atom. It can be concluded that, based upon our results, the interstitial chemical bonding effect in Fe_4Z, which is related to the Fe-Z bonds, is mainly determined by the covalent feature of the Fe-Z bonds. The volume dependence of the magnetic moment (μ_{Loc}), the Fermi-contact hyperfine fields (H_{FC}), the isomer shifts (IS) at Fe sites in γ'-Fe_4N and in γ'-Fe_4E, is calculated, respectively. The contributions of the magneto-volume effect and the chemical bonding effect of the N atom to μ_{Loc}, H_{FC}, and IS, are also reported. [S0163-1829(96)09131-X]

I. INTRODUCTION

Recently the great interest on the interstitial atoms (such as N, C, etc.) in magnetic materials is accelerated by the discovery of Sm-Fe-N.[1] Though a lot of works have been done up to date, there are still a few questions in the field to be clarified. For instance, the reason that the insertion of a little N atom in Sm_2Fe_{17} retains the lattice structure while it induces remarkable changes of intrinsic magnetic properties, is yet ambiguous, and one is usually confused by a $2.2\mu_B$ average iron magnetic moment in γ'-Fe_4N,[2] etc. Considering the structure of γ'-Fe_4N, in addition, the introduction of a N atom to the fcc(γ)-Fe lattice, observed experimentally, leads to an ~30% increase in volume (note that the experimental lattice parameter of the γ'-Fe_4N is 7.170 13 a.u.), and to two inequivalent Fe sites, say, the corner sites (Fe^{I}) and the face-centered sites (Fe^{II}). The interaction between the Fe^{I} and Fe^{II} sites was determined to be ferromagnetic. People therefore want to know why the Fe^{I} sites, with a magnetic moment of $2.98\mu_B$,[2] couples ferromagnetically with the Fe^{II} sites, with that of $2.01\mu_B$,[2] when a N atom is inserted into the octahedral interstitial site of the γ-Fe in which the Fe-Fe interaction is antiferromagnetic and thereby leads to paramagnetic behaviors at room temperature. These questions are necessarily related to the effect of a nonmetal interstitial atom inserted into a magnetic material.

On the basis of experiments Zhou *et al.*[3] suggested that the effects produced by interstitials could be decomposed into two parts: the magnetic volume effect and the chemical bonding effect. The contribution from the former to the magnetism is positive, while that from the latter is negative. The competition between them determines the final magnetic properties. Li *et al.*[4] have investigated, by the high pressure Mössbauer spectroscopy, the interstitial effects in $Gd_2Fe_{17}C_x$, and concluded that the chemical bonding effect is about 24% of the magnetic volume effect on the contribution to the average isomer shift ($\overline{\text{IS}}$) at Fe sites. Theoretically Beuerle and Fähnle[5] have discussed the competing effect of volume expansion and hybridization between the interstitial atoms and the neighboring Fe atoms in $Y_2Fe_{17}Z$ (Z=H, C, N). To investigate the effects of interstitial atoms, the Fe-N system with its simple crystal structure, such as the interstitial iron nitride Fe_4N with cubic symmetry, will be more convenient. We have experimentally studied the volume dependence of hyperfine parameters of γ'-Fe_4N by using high pressure Mössbauer spectroscopy.[6–8] The self-consistent band methods have been used to calculate the electronic structure of Fe_4N,[9–13] giving the numerical results of hyperfine parameters.[9–13] Sakuma[12] has already discussed the influence of the volume expansion on the magnetic moment. In addition, Coey and Qi (Ref. 14) have also obtained some valuable results for the effects of $2p$ interstitials in Fe but no detail results were presented.

To investigate the influences of the interstitial Z atoms on electronic structure and hyperfine interactions in this paper, the self-consistent spin-polarized linear muffin-tin orbitals (LMTO) band calculations are performed on the γ'-Fe_4Z (Z=H, C, N) and the γ'-Fe_4E which is γ'-Fe with an empty sphere insertion. Moreover, we calculate the volume dependence of the magnetic moment (μ_{Loc}), the Fermi-contact hyperfine fields (H_{FC}), and the isomer shifts (IS) at Fe sites in γ'-Fe_4N and γ'-Fe_4E, respectively. Based upon our calculated results, the magneto-volume and the chemical bonding effect of N are discussed in detail. To our knowledge, this is the first time the detail theoretical results on these magnetic systems using the LMTO mothod are presented.

The rest of the paper is organized as follows. We describe briefly the LMTO mothod and calculation techniques in Sec. II. Section III presents the calculated results of the chemical bonding effect of Z ztoms on electronic structures and hyperfine interactions of γ'-Fe_4Z (Z=H, C, N). Section IV gives the results of the magneto-volume effect on the magnetic moments, the Fermi-contact hyperfine fields, and the isomer shifts of these systems. The concluding remarks are given in Sec. V.

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II. LMTO METHOD

The LMTO method is elegantly described and reviewed in Refs. 15 and 16. We here perform a semirelativistic spin-polarized band calculation on the γ'-Fe_4Z system with the structure and coordinates of γ'-Fe_4N, using the LMTO method. The merits and disadvantages of the method, as well as the technique details, refer to Refs. 15 and 16. In our calculation, the exchange-correlation term is taken as the form deduced by von Barth and Hedin.[17] The Brillouin-zone integration is carried out for 286 $\vec{k}$ points in the irreducible zone. For valence electrons, we employ $3d$, $4s$, and $4p$ orbitals for Fe atoms, and s,p orbitals for Z atoms. The convergence is assumed when the root-mean-square error of the self-consistent potential is smaller than 1 mRy.

In the atomic-sphere-approximation the atomic radius assigned to the atomic sites should be chosen so as to satisfy $V=(4\pi/3)\,\Sigma_i Q_i S_i^3$ where V is the volume of a primitive cell and S_i is the atomic radius of the equivalent Q_i atoms in the cell. For Fe_4Z, the values of $S_{\mathrm{Fe^I}}$, $S_{\mathrm{Fe^{II}}}$, and S_Z must be well chosen. We take $S_{\mathrm{Fe^I}}=S_{\mathrm{Fe^{II}}}=S_{\mathrm{Fe}}$, in addition to $p=S_Z/S_{\mathrm{Fe}}=0.62$. So the values of S_{Fe} and S_Z are automatically defined by the above equation in accordance with the cell volume.

The calculations are performed for the following.

(1) $Fe_4Z(Z=H, C, N)$ with the coordinates of γ'-Fe_4N at the experimental lattice constant of γ'-Fe_4N.

(2) γ-Fe at the experimental lattice constant of γ'-Fe_4N but with an empty sphere (E) at the body-centered site ($S_E/S_{\mathrm{Fe}}=0.62$). The results represent the effect of volume-expansion produced by the Z atom. So the difference between the results of (1) and (2) indicates the chemical bonding effect of the Z atom.

(3) γ'-Fe_4N with various lattice parameter. We choose ten points for the calculation so that the volume variance between adjacent points is 10% of the volume expansion $\triangle V$ from γ-Fe to γ'-Fe_4N.

(4) γ'-Fe_4E with the same lattice parameter used in (3). But we only self-consistently calculate the first four points. The results represent the effect of volume expansion by the N atom with various lattice parameters. Therefore the difference between the results of (3) and (4) indicates the chemical bonding effect of N in γ'-Fe_4N under pressure.

The H_{FC} and IS are calculated according to the prescription given by Akai *et al.*[18]

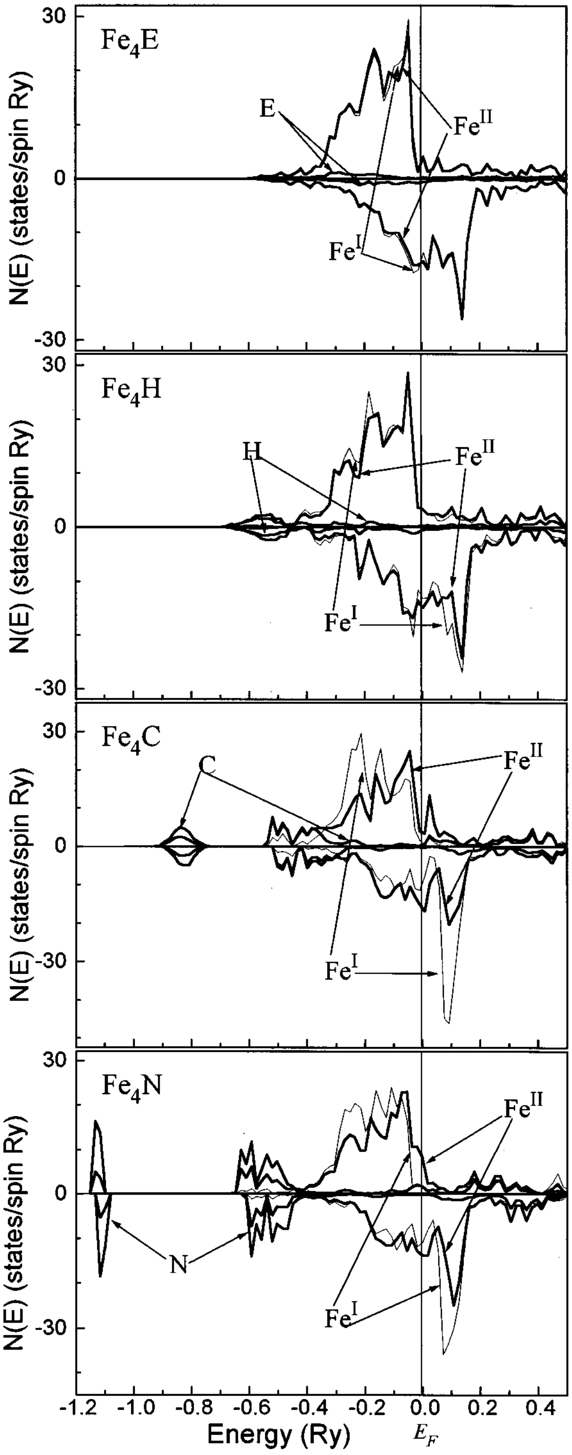

FIG. 1. The local DOS at each site in Fe_4E and Fe_4Z ($Z=H$, C, N).

III. CHEMICAL BONDING EFFECT OF Z ATOMS

A. Electronic structure

The density of states (DOS) at each site for Fe_4Z and Fe_4E are shown in Fig. 1. As can be seen, the interaction between Fe^{II} and Z is strong, since there is a considerable overlap between the states of valence electrons at Fe^{II} sites and those at the Z site, in contrast to that between the Fe^{I} site and the Z site (very weak). The higher the atomic number of the Z atom (from H to N) is, the deeper the electronic potential of the Z atom. Thus, the peaks of DOS corresponding to the Z site gradually shift to lower energy levels, and the electronic states between Fe and Z are pulled down to the lower energy levels. Compared with that in Fe_4E, the energy levels of $3d$ electrons at both Fe^{I} and Fe^{II} sites in Fe_4Z are changed, and the DOS at the Fermi level E_F, $N(E_F)$, is hence affected. So the linear coefficient of the electronic specific heat γ is also changed. The variations depend on the Z atom. In Fe_4H a decrease of $N(E_F)$ at both Fe^{I} and Fe^{II} sites occurs, whereas in Fe_4C and Fe_4N $N(E_F)$ at Fe^{II} increases. The dependence of $N(E_F)$ at Fe sites and the total γ on the Z atoms can be found in Table I. The insertion of the Z atom decreases the occupation number of spin down 3 d electrons at Fe^{I} but increases that at Fe^{II}, and thus affects

TABLE I. Calculated parameters of spin-polarized Fe_4Z (Z=H, C, N, E). Here μ_{Fe} in μ_B, $N(E_F)$ in states/atom spin Ry, γ in mJ/mol K^2.

	μ_{Fe}			N(E_F)		
	Fe^I	Fe^{II}	average	Fe^I	Fe^{II}	
Fe_4E	2.61	2.66	2.65	19.6	19.3	13.6
Fe_4H	2.75	2.40	2.49	16.1	17.6	12.1
Fe_4C	3.27	1.54	1.97	10.5	21.3	13.0
Fe_4N	3.16	2.06	2.33	12.0	22.2	13.9

the magnetic moments μ_{Fe} at the Fe sites. The changes of the μ_{Fe} with Z are also given in Table I. It can be observed that the chemical bonding effect of Z increases the magnetic moment at the Fe^I site and decreases that at the Fe^{II} site. The combined effect at Fe^I and Fe^{II} sites prevents an increase of the exchange splitting in the unit cell and thus reduces the average magnetic moment at Fe sites. Obviously the effect of the C atom is the most remarkable in the series Z=H, C, N.

Summarizing the influence of Z on the electronic structure at Fe sites, we find that the chemical bonding effect of Z is different, and changes irregularly with the increase of the atomic number of Z. The effect of the H atom is the weakest, while that of C is larger than that of the N atom. It is well known that the properties of C, which is the element with characters of both metal and nonmetal, are different from those of H and N, where H is similar to a metal, and the electronegativity of N is strong. In turn there are more metallic and ionic features in Fe-H and Fe-N bonds, respectively, while the Fe-C bond is more like a covalent bond. This suggests that the different properties of Fe-Z bonds stem from the difference of the chemical bonding of the Z atom. In accordance with our results, it is implied that the chemical bonding effect of Z is mainly determined by the covalency of the Fe-Z bond.

B. Hyperfine interaction

Figure 2(a) shows the chemical bonding effect of Z on the H_{FC} at Fe sites. Compared with that in Fe_4E, the chemical bonding effect of Z reduces the average H_{FC} at Fe sites. The reduction in Fe_4C is the largest. Considering the H_{FC} at the Fe^I and Fe^{II} sites, respectively, we find that the chemical bonding effects of H and C strongly reduce the H_{FC} at both Fe^I and Fe^{II} sites, while that of N increases H_{FC} at the Fe^I site. In order to compare the chemical bonding effects of different Z atoms on H_{FC}, we decompose H_{FC} into the two parts, H_{FC}^{core}, which is the contribution of core electrons and comes from the polarization of core due to the polarized d electrons, and H_{FC}^{val}, which comes from the polarization of valence electrons. The H_{FC}^{core} and H_{FC}^{val} contributions of H_{FC} are shown in Fig. 2(a), which illustrates that H_{FC}^{core} at Fe sites is the dominant contribution to H_{FC}. The μ_{Loc} dependence of the H_{FC}, H_{FC}^{core}, and H_{FC}^{val} at Fe sites, is shown in Fig. 2(b), respectively. Obviously a linear relation between the H_{FC}^{core} and the local magnetic moment at Fe sites is observed, and the proportional coefficient is estimated to be about -13 T/μ_B. Thus it can be seen that H_{FC} at Fe sites is affected by two factors, μ_{Loc} and the polarization of the valence electrons.

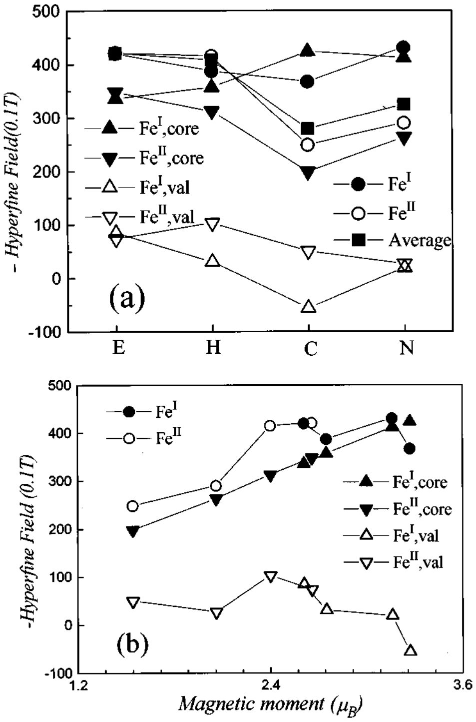

FIG. 2. The calculated H_{FC} in Fe_4E and Fe_4Z (Z=H,C,N). (a) The H_{FC} at Fe sites, and the core and valence contributions of H_{FC}. (b) The dependence of the H_{FC} at Fe sites on $\overline{\mu_{Fe}}$ and dependence of the H_{FC}^{core} and H_{FC}^{val} at Fe sites on μ_{Fe}.

Although the H_{FC}^{val} contribution to H_{FC} is small, it affects the interaction between atoms. H_{FC}^{val} consists of two parts, the local valence contribution $H_{FC}^{l,val}$ which comes from the s-d exchange interaction within the atom and is proportional to the local magnetic moment (μ_s) of s electrons, and the transferred hyperfine magnetic field $H_{FC}^{t,val}$ which comes from the s-d hybridization between s orbitals of the atom and the spin-polarized d orbitals of the neighboring atoms. Since the μ_s at Fe sites is very small, the $H_{FC}^{l,val}$ contribution to H_{FC}^{val} is weak so that a considerable H_{FC}^{val} at these sites might reveal a strong s-d hybridization between Fe^I and Fe^{II} sites. In contrast to Fe_4E, the chemical bonding effect of H and C changes the s-d hybridization between Fe^I and Fe^{II} sites. This results in an increase of the H_{FC}^{val} at Fe^{II} produced by the hybridization between s orbitals at Fe^{II} and spin-polarized d orbitals at Fe^I. At Fe^I, however, the hybridization between s orbitals at the Fe^I site and spin-polarized d orbitals at the Fe^{II} site has a small effect on H_{FC}^{val}. It should be noted that the chemical bonding effect of C decreases H_{FC}^{val} at Fe^{II} and furthermore changes H_{FC}^{val} at Fe^I from a negative value to a positive value. Indeed this also indicates the strong chemical bonding effect of the C atom, which changes the direction of exchange splitting at Fe^I induced by the s-d hybridization with the neighboring Fe atoms.

The H_{FC} at the Z site is listed in Table II. It can be seen that the main source of H_{FC} at the Z site is H_{FC}^{val} in which $H_{FC}^{t,val}$ transferred from the neighboring atoms dominates. The

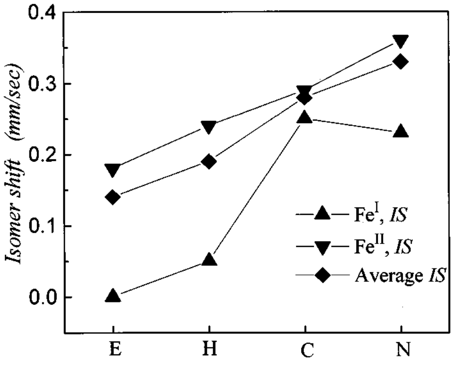

FIG. 3. The Mössbauer isomer shift IS relative to α-Fe at Fe sites and the average IS in Fe_4E and Fe_4Z $(Z=H, C, N)$.

difference in H_{FC} at Z sites reveals that the Fe-Z interaction varies strongly with the Z atoms. Generally speaking, a positive contribution to the H_{FC}^{val} at Z sites is induced by antibonding states and a negative one by bonding states, where both are produced by the s-d hybridization. Our results indicate that the bonding states are favored in the Fe-H bonds while the antibonding states dominate in the Fe-C and Fe-N bonds. Furthermore, the antibonding states in Fe-N are stronger than those in the Fe-C. This agrees with the results quoted by Akai.[18]

Moreover, we can discuss the chemical bonding effect of the Z atom from the IS at Fe sites. The calculated results relative to that of α-Fe are given in Fig. 3, with the calibration constant $\alpha=-0.24a_0^3$ mm sec^{-1}. As can be seen from this figure, the chemical bonding effect of the Z atom promotes the mobility of the electrons, and then in turn decreases the s-like charge density at the Fe nucleus, so the IS at Fe sites are increased.

Although we did not perform calculations for many Z atoms in Fe_4Z, it is reasonable to state, at least qualitatively, that the chemical bonding effect of the Z atom increases with the atomic number of Z at the C atom. Here we like to point out that, since the experimental data on this aspect are rare, a thoroughly quantitative comparison between the theoretical and experimental results is not available at the moment. Nevertheless we can make a comparison between our calculated results for Fe_4N and the corresponding experimental results. Although there are some quantitative errors, they agree qualitatively well.

IV. MAGNETO-VOLUME EFFECT AND THE CHEMICAL BONDING EFFECT OF N ATOMS

TABLE II. Calculated Fermi-contact hyperfine field H_{FC} in kG at Z sites and its core and valence contributions for Fe_4Z.

	H_{FC}	H_{FC}^{val}	H_{FC}^{core}
H	-6.2	-6.2	0
C	16.4	10.4	6.0
N	15.8	22.8	-7.0

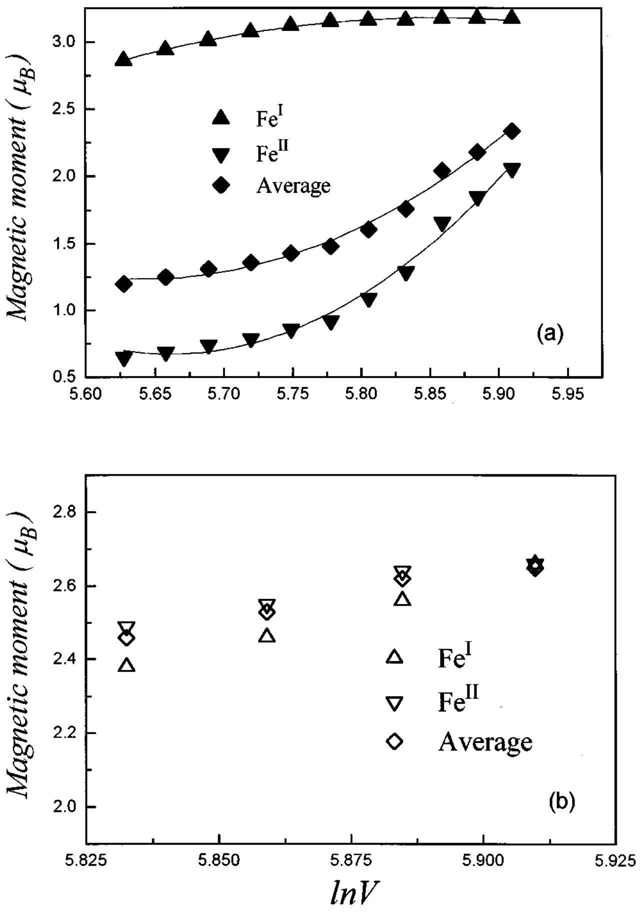

FIG. 4. The local magnetic moment μ_{Fe} at Fe sites and the average magnetic moment $\overline{\mu_{Fe}}$ in (a) γ'-Fe_4N and (b) γ'-Fe_4E as a function of the unit cell volume.

As a function of the unit cell volume, $\overline{\mu_{Fe}}$ and μ_{Fe} at Fe sites in γ'-Fe_4N and γ'-Fe_4E are calculated, respectively, as shown in Fig. 4. As mentioned above, the variation of μ_{Fe} at Fe sites in Fig. 4(b) represents the volume dependence of the contribution of the magneto-volume effect which broadens the $3d$ subbands of Fe and reduces the $3d$ exchange splitting with the decrease of unit cell volume, while those in Fig. 4(a) indicate the volume dependence of the combined contribution of the magneto-volume effect and the chemical bonding effect. Therefore in Fig. 4 there is a great decrease of average Fe magnetic moment with decreasing unit cell volume, but the scale of the decrease in Fig. 4(b) is less than that in Fig. 4(a). Due to the combination of the magneto-volume and the chemical bonding effect, the $\mu_{Fe^{II}}$ decreases more rapidly with volume compression than the μ_{Fe^I} in Fig. 4(a), i.e., μ_{Fe^I} in γ'-Fe_4N is more stable against the lattice compression, in constrast to that in γ'-Fe_4E.

In spite of nonlinear dependence of the magnetic moment at Fe sites on the unit cell volume, we use the formula

$$\ln\mu(V)=A+B\ln V$$

to fit the volume dependence of magnetic moment at Fe sites. The fitting results show that, in γ'-Fe_4N the magnetic moments decrease with decreasing the unit cell volume by $\partial\ln\mu_{Fe^I}/\partial\ln V=0.34$ at the Fe^I site and by $\partial\ln\mu_{Fe^{II}}/\partial\ln V=4.26$ at the Fe^{II} site. Here there is a discrepency between our calculated results and the experimental results of Lord *et al.*,[19] in which the volume dependence of the

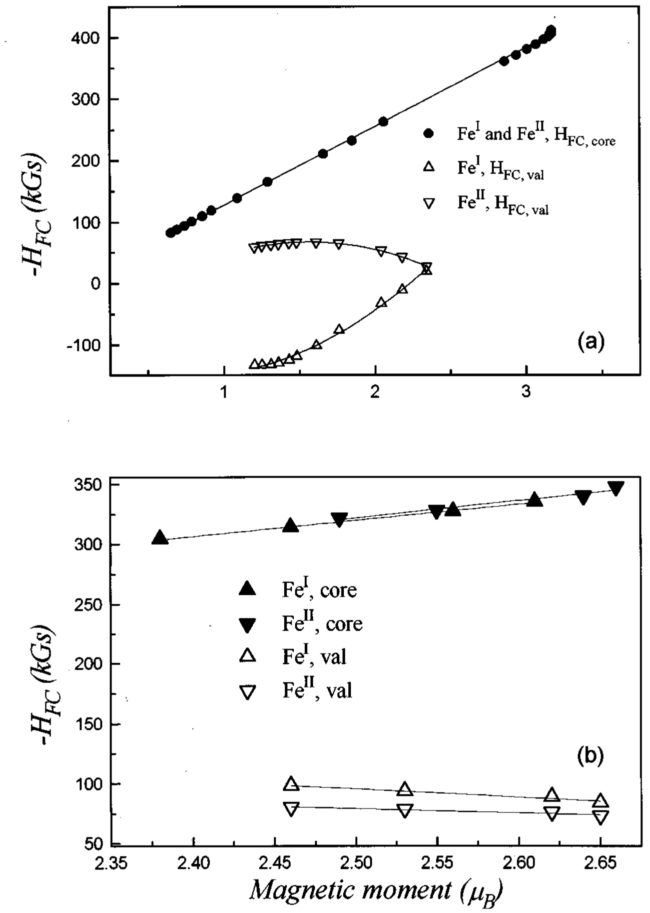

FIG. 5. The $\mu_{\rm Fe}$ dependence of $H_{\rm FC}^{\rm core}$ at Fe sites and the $\overline{\mu}$ dependence of $H_{\rm FC}^{\rm val}$ at Fe sites in (a) γ'-Fe$_4$N and (b) γ'-Fe$_4E$.

magnetization for Fe$^{\rm I}$ and Fe$^{\rm II}$ are found to be nearly the same and much larger. Comparing with that in γ'-Fe$_4E$, in which the volume compression effect decreases the magnetic moments by $\partial\ln\mu_{\rm Fe^I}/\partial\ln V=1.45$ and $\partial\ln\mu_{\rm Fe^{II}}/\partial\ln V=0.91$, we can obtain the contribution of the chemical bonding effect of N to $\mu_{\rm Fe}$, by $\partial\ln\mu_{\rm Fe^I}/\partial\ln V=-1.11$ and by $\partial\ln\mu_{\rm Fe^{II}}/\partial\ln V=3.35$.

With decreasing the unit cell volume, the $H_{\rm FC}$ at Fe sites in γ'-Fe$_4$N decreases rapidly. We fit the logarithmic $H_{\rm FC}$ at Fe sites in γ'-Fe$_4$N as a function of the unit cell volume. The logarithmic volume derivative $\partial\ln|H_{\rm FC}|/\partial\ln V$ of the magnitude of the average $H_{\rm FC}$ at Fe sites is found to be $\partial\ln|\overline{H}_{\rm FC}|/\partial\ln V=2.54$, which agrees well with the experimental result at 4.2 K.[7] For Fe$^{\rm I}$ and Fe$^{\rm II}$ sites, $\partial\ln|H_{\rm Fe^I}|/\partial\ln V=2.26$ and $\partial\ln|H_{\rm Fe^{II}}|/\partial\ln V=2.68$ are obtained, respectively. Unfortunately, they do not agree with the experimental results at 4.2 K. It is probably suggested that the dipole field has also played a role under high pressure due to the weakened cubic symmetry. We fit the logarithmic $H_{\rm FC}$ at Fe sites in γ'-Fe$_4E$, and obtain the contribution of the magneto-volume effect to the logarithmic volume derivative of $H_{\rm FC}$, $\partial\ln|H_{\rm Fe^I}|/\partial\ln V=0.56$ and $\partial\ln|H_{\rm Fe^{II}}|/\partial\ln V=0.61$. Similarly the contribution of the chemical bonding effect to the logarithmic volume derivative can be deduced to be $\partial\ln|H_{\rm Fe^I}|/\partial\ln V=1.70$ and $\partial\ln|H_{\rm Fe^{II}}|/\partial\ln V=2.07$. In constrast to the contribution to $\mu_{\rm Fe}$, the chemical bonding effect of N decreases the $H_{\rm FC}$ at Fe sites.

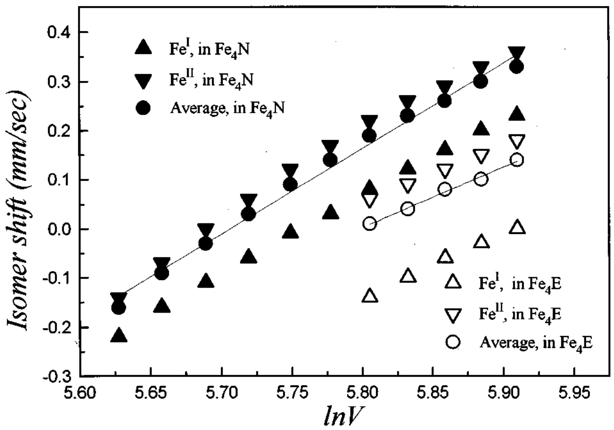

FIG. 6. The volume dependence of IS at Fe sites and the average IS in γ'-Fe$_4$N and γ'-Fe$_4E$.

In order to understand the discrepancy between changes of $\mu_{\rm Fe}$ and $H_{\rm FC}$ at Fe sites due to the chemical bonding effect, we decompose $H_{\rm FC}$ into $H_{\rm FC}^{\rm core}$ and $H_{\rm FC}^{\rm val}$ as before. The $\mu_{\rm Fe}$ dependence of $H_{\rm FC}^{\rm core}$ at Fe sites in γ'-Fe$_4$N and γ'-Fe$_4E$ are shown in Fig. 5(a) and Fig. 5(b), respectively. For γ'-Fe$_4$N and γ'-Fe$_4E$ the proportional coefficient A between $H_{\rm FC}^{\rm core}$ and μ_{Fe} at Fe sites can be estimated to be -12.7 T/μ_B and -13.9 T/μ_B, respectively. According to the results, it may be suggested that the chemical bonding effect of N atoms tends to reduce the value of A.

In γ'-Fe$_4$N, $H_{\rm FC}^{t,\rm val}$ at the Fe$^{\rm II}$ site, which has a weakly negative contribution to $H_{\rm FC}$, changes little with decreasing the unit cell volume, while that at Fe$^{\rm I}$ site increases greatly with the decreasing of the unit cell volume, and changes into a remarkably positive contribution to $H_{\rm FC}$. In γ'-Fe$_4E$, all the $H_{\rm FC}^{t,\rm val}$ at Fe$^{\rm I}$ and Fe$^{\rm II}$ sites are negative contributions to $H_{\rm FC}$. Usually, $H_{\rm FC}^{t,\rm val}$ is proportional to $\overline{\mu}$ of atoms,[20]

$$H_{\rm FC}^{\rm val}=B\overline{\mu},$$

depending upon the interactions between the atom and its neighbors. $H_{\rm FC}^{t,\rm val}$ reveals the influence of the Fe-neighbors on H_{FC} by the hyperfine-coupling coefficient B. $H_{FC}^{t,val}$ at Fe sites in γ'-Fe$_4$N and γ'-Fe$_4E$ are also computed as functions of $\overline{\mu}_{\rm Fe}$, as shown in Fig. 5. The nonlinear variation of $H_{\rm FC}^{t,\rm val}$ at Fe sites with $\overline{\mu}_{\rm Fe}$ indicates the change of the coefficient B with decreasing the unit cell volume, and thereby reveals the change of the interactions between Fe and its neighbors. Fitting the volume dependence of B at Fe sites in γ'-Fe$_4$N and γ'-Fe$_4E$, we can obtain $\partial B_{\rm Fe^I}/\partial\ln V=-44$ T/μ_B and $\partial B_{\rm Fe^{II}}/\partial\ln V=12$ T/μ_B for γ'-Fe$_4$N, and $\partial B_{\rm Fe^I}/\partial\ln V=13$ T/μ_B and $\partial B_{\rm Fe^{II}}/\partial\ln V=8$ T/μ_B for γ'-Fe$_4E$. The chemical bonding effect indeed inverses the sign of $\partial B/\partial\ln V$ at the Fe$^{\rm I}$ site, and shows that the change of interactions between Fe$^{\rm I}$ and its neighbors with decreasing the unit cell volume is greatly different from that of between Fe$^{\rm II}$ and its neighbors. So we suggest that it is the chemical bonding effect of N that results in the discrepancy between the volume dependence of $\mu_{\rm Fe}$ and $H_{\rm FC}$ at Fe sites in γ'-Fe$_4$N by changing the interactions between Fe and its neighbors.

Finally we present the calculated volume dependence of IS at Fe sites in γ'-Fe$_4$N and γ'-Fe$_4E$, as shown in Fig. 6. With decreasing the unit cell volume, the combined effect of the volume compression of 4s electrons and the enhancement of Fe$^{\mathrm{I}}$-Fe$^{\mathrm{II}}$ and Fe-N s-d hybridizations in γ'-Fe$_4$N increases the charge density $\rho(0)$ at the Fe nucleus, and therefore decreases IS at Fe sites rapidly. Fitting the variation of IS at Fe sites, we can obtain $\partial \mathrm{IS}_{\mathrm{Fe}^{\mathrm{I}}}/\partial \ln V = 1.59$ mm/sec and $\partial \mathrm{IS}_{\mathrm{Fe}^{\mathrm{II}}}/\partial \ln V = 1.76$ mm/sec, which agree well with the experimental results.[7] While in γ'-Fe$_4E$ we can also find $\partial \mathrm{IS}_{\mathrm{Fe}^{\mathrm{I}}}/\partial \ln V = 1.34$ mm/sec and $\partial \mathrm{IS}_{\mathrm{Fe}^{\mathrm{II}}}/\partial \ln V = 1.15$ mm/sec, which are only due to the magneto-volume effect of a N atom. We can therefore regard the IS changes, $\partial \mathrm{IS}_{\mathrm{Fe}^{\mathrm{I}}}/\partial \ln V = 0.25$ mm/sec and $\partial \mathrm{IS}_{\mathrm{Fe}^{\mathrm{II}}}/\partial \ln V = 0.61$ mm/sec, as a result of the chemical bonding effect of N atom.

V. CONCLUDING REMARKS

The spin-polarized LMTO method has been applied to calculate the electronic bands of γ'-Fe$_4Z$ (Z=H, C, N) and γ'-Fe$_4E$ which corresponds to γ-Fe with an empty sphere. The effects of the interstitial Z atoms have been explored.

The insertion of the Z atom promotes the mobility of the electrons and then prevents an increase of the exchange splitting. The chemical bonding of the Z atom changes the Fe-Fe interaction, resulting in drastic changes of the electronic structure and hyperfine parameters at Fe sites. The Fe-Z interaction depends on Z, among all situations studied, the chemical bonding effect of the C atom is the most remarkable. In accordance with our results, it can be concluded that the interstitial chemical bonding effect in Fe$_4Z$ is dominated by the covalent feature of Fe-Z bonds.

According to the calculated volume dependence of μ_{Loc}, H_{FC} and IS at the Fe site in γ'-Fe$_4$N, the magneto-volume effect and the chemical bonding effect of a N atom have been discussed and decomposed. Due to the chemical bonding effect of a N atom, a discrepancy between the volume dependences of magnetic moment and H_{FC} at Fe sites in γ'-Fe$_4$N occurs.

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