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A linear muffin-tin orbital calculation of the volume dependence of local electronic and magnetic properties of γ' -Fe₄N

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Abstract. The volume dependence of local electronic and magnetic properties of γ' -Fe₄N has been investigated using the self-consistent spin-polarized linear muffin-tin orbital (LMTO) calculation. The results obtained indicate that the Fe magnetic moment at the face-centred sites (Fe^{II}) decreases more rapidly than that at the corner sites (Fe^I) with decreasing unit-cell volume. The decrease of Fermi-contact hyperfine field (H_{FC}) at Fe sites with the decrease of the unit-cell volume not only results from the corresponding decrease of the Fe magnetic moment, but also is affected by the abnormal change of the transferred H_{FC} ($H_{FC}^{t, val}$) at these sites. The discussion on $H_{FC}^{t, val}$ at Fe sites partly reveals the unit-cell volume dependence of hyperfine interactions among atoms. Moreover the change of the calculated Mössbauer isomer shift (IS) at Fe sites with decreasing unit-cell volume is in agreement with the experimental results.

1. Introduction

Recently, there has been a great deal of interest in the study of the electronic structure and magnetic properties of iron nitrides (such as γ' -Fe₄N [1–3]). Regarding the structure of γ' -Fe₄N, the introduction of N to the fcc (γ)-Fe lattice leads to an $\sim 30\%$ increase (the experimental lattice parameter of γ' -Fe₄N is 7.170 13 au) in volume and to two inequivalent Fe sites, i.e. the corner sites (Fe^I) and the face-centred sites (Fe^{II}). The Fe^I sites each carry a large magnetic moment ($\mu = 2.98\mu_B$) [4] with little interaction with N, while the Fe^{II} sites with a small magnetic moment ($\mu = 2.01\mu_B$) [4] bond strongly with N atoms. The Fe^I atoms couple ferromagnetically with the Fe^{II}.

In view of the large lattice expansion associated with the formation of γ' -Fe₄N, and the very different bonding of Fe^I and Fe^{II} sites, it is particularly interesting to investigate their electronic and magnetic properties as a function of volume (or pressure). Recently Li *et al* [5] and Yang *et al* [6] have investigated the local electronic and magnetic properties of γ' -Fe₄N using the high-pressure Mössbauer effect (ME) technique at 300 K and 4.2 K, respectively. Lord *et al* [2] have measured the volume dependence of the magnetization and NMR of γ' -Fe₄N. Theoretically, there are many contributions to the volume dependence of local properties in γ' -Fe₄N; for example, Sakuma [7] has already discussed the influence of the volume expansion on the magnetic moment, and Paduani and Krause [1] have also calculated the lattice spacing dependence of the magnetic hyperfine field (H_{hf}), the isomer shift (IS) and the magnetic moment using the DVM method. It is found that the volume dependences of the magnetic moments and the hyperfine fields at Fe^I and/or Fe^{II} sites are different, but the reasons for this are not quite clear.

For the above purposes, in the present paper we have calculated the volume dependences of local electronic and magnetic properties in γ' -Fe₄N using the self-consistent LMTO method, and discussed the changes of the interactions between atoms with decreasing unit-cell volume.

2. The method of calculation

The LMTO method [8, 9] has been employed to perform a semi-relativistic spin-polarized band calculation for the γ' -Fe₄N system for various unit-cell volumes. The exchange–correlation term was taken as the form deduced by von Barth and Hedin [10]. The Brillouin zone integration was carried out for 286 k -points in the irreducible zone. We have employed the orbitals up to $l = 2$ for 3d and 4s electrons of Fe atoms, and s, p orbitals for 2s, 2p electrons of N atoms. The convergence is assumed to have been achieved when the root mean square error of the self-consistent potential is better than 1 mRyd.

In the atomic-sphere approximation (ASA) the atomic radius assigned to the atomic sites should be chosen so as to satisfy

$$V = \frac{4\pi}{3} \sum_i Q_i S_i^3$$

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 Fe₄N, therefore, the values of S_{Fe^I} , $S_{Fe^{II}}$ and S_N must be chosen. We have taken $S_{Fe^I} = S_{Fe^{II}} = S_{Fe}$, and in addition $p = S_N/S_{Fe} = 0.62$. So the values of S_{Fe} and S_N are automatically defined by the above equation in accordance with the cell volume.

We have chosen ten points for calculation so that the volume decrease between adjacent points is 10% of the volume expansion ΔV on going from γ -Fe to γ' -Fe₄N. The Fermi-contact magnetic hyperfine fields (H_{FC}) and Mössbauer isomer shifts (IS) have been calculated according to the prescription given by Akai *et al* [11].

3. Results and discussion

The average Fe magnetic moment and the local magnetic moments at Fe sites in γ' -Fe₄N are shown as functions of unit-cell volume in figure 1(a). With the unit-cell compression, the 3d subbands for Fe are broadened and the 3d exchange splitting reduced, and thus there is a great decrease of the average Fe magnetic moment. Moreover, the Fe–N interactions [12], which reduce the magnetic moment at Fe^{II} sites but raise the magnetic moment at Fe^I sites, are greatly increased with the decrease of unit-cell volume. Therefore the magnetic moment at an Fe^{II} site decreases more rapidly than that at an Fe^I site, i.e. the magnetic moment at an Fe^I site is more stable against the compression of the lattice. In spite of the non-linear dependence of the magnetic moment at Fe sites on the unit-cell volume, we have used the formula

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

to fit the magnetic moment at Fe sites. The fitting results show that $\partial \ln \mu_{Fe^I} / \partial \ln V = 0.34$ for Fe^I sites and $\partial \ln \mu_{Fe^{II}} / \partial \ln V = 4.26$ for Fe^{II} sites. For the average Fe magnetic moment, we have also obtained $\partial \ln \bar{\mu} / \partial \ln V = 2.00$.

With the decrease of unit-cell volume, H_{FC} at Fe sites decreases rapidly. We have illustrated the logarithmic H_{FC} at Fe sites in figure 1(b) as a function of unit-cell volume, and the logarithmic volume derivative $\partial \ln |H_{FC}| / \partial \ln V$ of the magnitude of the average

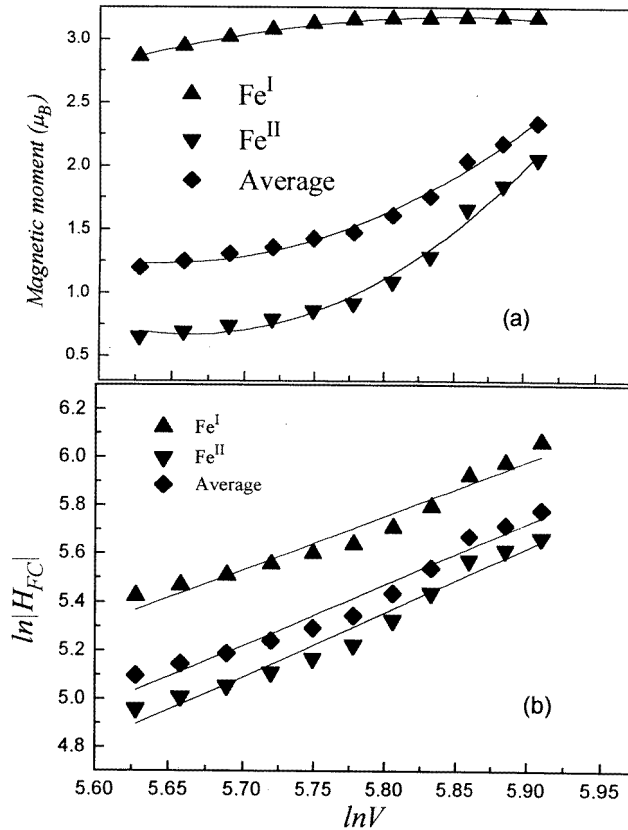


Figure 1. (a) The magnetic moments at Fe sites and average magnetic moments in γ' -Fe₄N as functions of unit-cell volume. (b) The volume dependences of the H_{FC} at Fe sites and the average H_{FC} in γ' -Fe₄N.

H_{FC} at Fe sites is found to be $\partial \ln |\overline{H_{FC}}| / \partial \ln V = 2.54$. For Fe^I and Fe^{II} sites, $\partial \ln |H_{Fe^I}| / \partial \ln V = 2.26$ and $\partial \ln |H_{Fe^{II}}| / \partial \ln V = 2.68$ are obtained respectively. In contrast to the changes of magnetic moments at Fe^I and Fe^{II} sites with decreasing unit-cell volume, it has been noted that the values of $\partial \ln |H_{FC}| / \partial \ln V$ are almost the same for Fe^I and Fe^{II} sites.

In order to understand the discrepancy between the changes of magnetic moment and H_{FC} at Fe sites, we decompose H_{FC} into H_{FC}^{core} and H_{FC}^{val} , which are the contributions of core and valence electrons, respectively. H_{FC}^{core} comes from the polarization of the core due to the polarized d electrons and is proportional to the local magnetic moment μ_l of the atom, while H_{FC}^{val} mainly comes from the contribution of the transferred magnetic hyperfine field ($H_{FC}^{t, val}$), which is induced by the sd hybridization between s orbitals of the atom and the spin-polarized d orbitals of the neighbouring atom, and is proportional to the average magnetic moment of atoms, i.e. [11, 13]

$$H_{FC} = H_{FC}^{core} + H_{FC}^{val} = A\mu_l + B\bar{\mu}.$$

The volume dependences of H_{FC}^{core} and H_{FC}^{val} at Fe sites are given in figure 2(a). It is shown that H_{FC}^{core} at Fe sites is the main contribution to H_{FC} and its volume dependence is similar to that of the magnetic moments shown in figure 1(a)—in contrast to the case

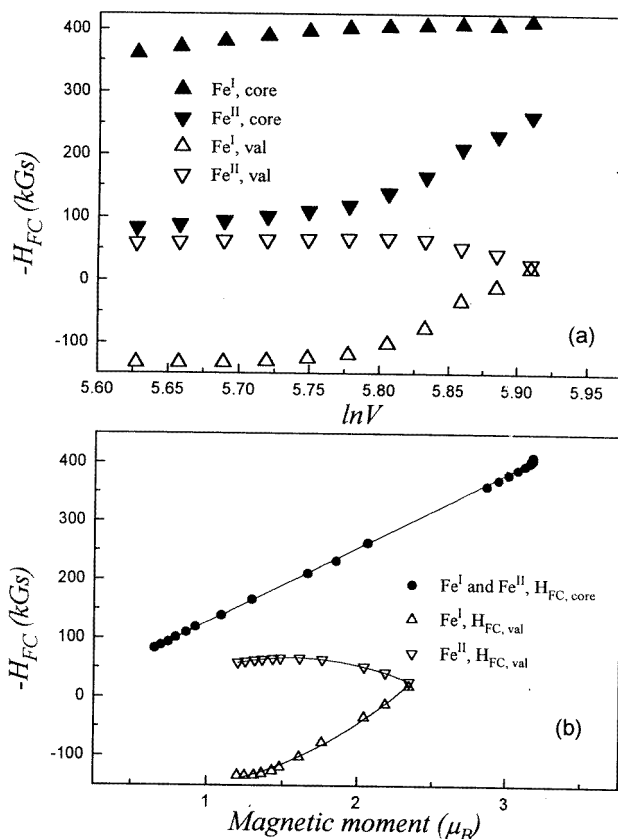


Figure 2. H_{FC}^{core} and H_{FC}^{val} at Fe sites in γ' -Fe₄N for various unit-cell volumes. (a) The volume dependences of H_{FC}^{core} and H_{FC}^{val} . (b) The local magnetic moment dependence of H_{FC}^{core} and the average magnetic moment dependence of H_{FC}^{val} .

for H_{FC}^{val} at Fe sites. The local magnetic moment dependence of the H_{FC}^{core} at Fe sites in γ' -Fe₄N is shown in figure 2(b). Obviously a linear relation between the H_{FC}^{core} and the local magnetic moment at Fe sites is observed and the proportionality coefficient is evaluated to be about $-12.7 \text{ T}/\mu_B$, i.e.

$$H_{FC}^{core} = -12.7\mu_l \quad (\text{T})$$

which is larger than that of Fe-based alloys [11, 14].

The change of $H_{FC}^{t, val}$ (approximately H_{FC}^{val}) at Fe sites with the unit-cell volume is quite different from that of H_{FC}^{core} . At Fe^{II} sites $H_{FC}^{t, val}$ is a small negative contribution to H_{FC} and changes little with decreasing unit-cell volume, while at Fe^I sites $H_{FC}^{t, val}$ increases greatly with the decrease of unit-cell volume and changes into a remarkable positive contribution to H_{FC} . As is indicated by the results of Mohn *et al* [15], $H_{FC}^{t, val}$ at Fe^I sites plays an important role in the volume dependence of H_{FC} at Fe^I sites and thereby produces the discrepancy between the changes of magnetic moment and H_{FC} at Fe sites with unit-cell volume.

As mentioned above, $H_{FC}^{t, val}$ at Fe sites is proportional to the average magnetic moment $\bar{\mu}$ in the unit cell and reveals the influence of the Fe neighbours on H_{FC} at Fe sites via the

hyperfine coupling coefficient B . The $H_{FC}^{t, val}$ at Fe sites in γ' -Fe₄N with various unit-cell volumes are also shown in figure 2(b) as functions of the average Fe magnetic moment. The non-linear variation of $H_{FC}^{t, val}$ at Fe sites with $\bar{\mu}$ indicates the change of the coefficient B with unit-cell volume and reveals the variation of the interactions between Fe and its neighbours. Fitting the changes of B at Fe^I and Fe^{II} sites with unit-cell volume, we have obtained $\partial B_{Fe^I}/\partial \ln V = -44.2 \text{ T}/\mu_B$ and $\partial B_{Fe^{II}}/\partial \ln V = 12.5 \text{ T}/\mu_B$. Indeed the opposite sign of $\partial B/\partial \ln V$ at Fe^I and Fe^{II} sites indicates that the variation of interactions between Fe^I and neighbours with unit-cell volume is different from that between Fe^{II} and neighbours.

Finally we discuss the volume dependence of IS at Fe sites. The calculated results relative to that for α -Fe are given in figure 3; the calibration constant is taken as $\alpha = -0.24a_0^3 \text{ mm s}^{-1}$. With decreasing unit-cell volume, the combined effect of the volume compression of 4s electrons and the enhancement of Fe^I-Fe^{II} and Fe-N sd hybridizations increases the density of charge $\rho(0)$ at the Fe nucleus and therefore decreases IS rapidly at Fe sites. Fitting the variation of IS, we obtained $\partial \bar{IS}/\partial \ln V = 1.73 \text{ mm s}^{-1}$ which agrees well with the experimental results at 300 K [5]. Moreover, we have obtained $\partial IS_{Fe^I}/\partial \ln V = 1.59 \text{ mm s}^{-1} < \partial IS_{Fe^{II}}/\partial \ln V = 1.76 \text{ mm s}^{-1}$.

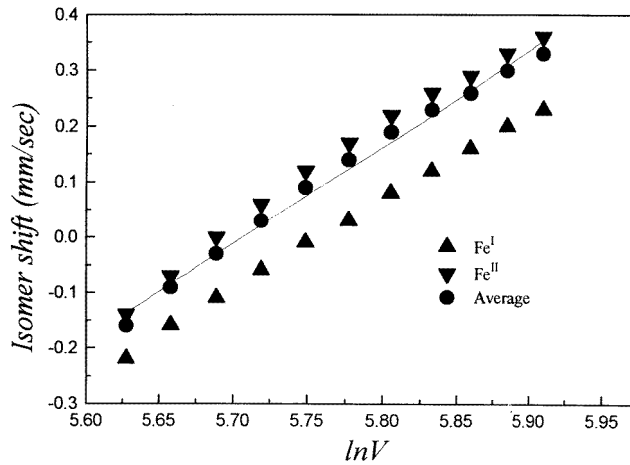


Figure 3. The volume dependence of IS at Fe sites and the average IS.

4. Conclusion

The spin-polarized linear muffin-tin orbitals (LMTO) method has been used to perform calculations for γ' -Fe₄N with various unit-cell volumes. The volume dependences of the local electronic and magnetic properties at Fe sites have been discussed.

It has been found that the Fe magnetic moments at Fe^I sites are more stable against the unit-cell compression than those at Fe^{II} sites. The decrease of H_{FC} at Fe sites with the decrease of unit-cell volume resulted from the combined effect of the corresponding decrease of the Fe magnetic moment and the change of $H_{FC}^{t, val}$ at Fe sites. Furthermore with decreasing unit-cell volume, the opposite signs of $\partial B/\partial \ln V$ at Fe^I and Fe^{II} sites indicate that the variation of interactions between Fe^I and its neighbours is different from that between Fe^{II} and its neighbours. The change of IS at Fe sites with decreasing unit-cell volume is in agreement with the experimental results at 300 K.

Acknowledgments

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