Magnetovolume and chemical bonding effects of Sn atom in the γ'-$(Fe_{1-x}Sn_x)_4N$ compounds

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Abstract Combining x-ray diffraction and high pressure Mössbauer spectroscopy, the structure and the hyperfine parameters of Sn substituted for Fe in γ'-Fe_4N were investigated. The results of x-ray diffraction indicate that single phase γ'-$(Fe_{1-x}Sn_x)_4N$ compounds can be synthesized in the composition range $0 \leq x \leq 0.3$, and the lattice parameter can be well fitted with two linear formulas $\alpha_0(x) = 3.795 + 0.019 \times x\,(0.0 \leq x \leq 0.10)$ and $\alpha_0(x) = 3.795 + 0.228 \times (x - 0.1)\,(0.10 \leq x \leq 0.30)$ for different content of Sn. Using high pressure Mössbauer spectra, the influences of the magnetovolume effect and the chemical bonding effect of Sn atom on the hyperfine magnetic field and the isomer shift were first distinguished. It is found that the magnetovolume and the chemical bonding have different influences on the properties of γ'-$(Fe_{1-x}Sn_x)_4N$, and the latter plays a more important role.

Keywords Iron nitrides, Mössbauer spectroscopy, X-ray diffraction

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1 INTRODUCTION

It is known that solid solution is formed by introducing some additive atoms into a basic phase. Comparing with the original material, the new material formed by introducing interstitial atoms or substitutional atoms has been changed in the unit cell volume and the charge distribution. As the structure type retains the same before and after the introduction, the influence of introduced atom can be divided into two parts.[1] One is magnetovolume effect (MVE) which comes from the contribution of the changes of lattice size, and the other is chemical bonding effect (CBE) which is caused by the redistribution of charge. In order to understand the mechanism of introducing atom which improves the properties of materials, it is very important to distinguish the influence of the MVE and the CBE on the properties, and this is also very useful for searching new material from both interstitial and substitutional aspects.

From the previous research of the rare-earth metal compounds, the importance of the interstitial and substitutional atoms can be easily found.[2] In order to understand

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the effect of interstitial atoms, the MVE and CBE of interstitial atoms T (T=N,C) in $R_2Fe_{17}T$ compounds were investigated theoretically[3] and experimentally.[4] However, because of the complexity of the structure (too much atoms in one unit cell), it is not easy to get exact result, especially in the quantitative analysis. Therefore some people focus their attention on the γ'-Fe_4N type compounds with simpler structure.[5,6] Besides this reason, the γ'-Fe_4N type compounds that have higher saturation magnetization are a potential candidate of high-density magnetic recording material.[7–9] It is found experimentally that the introduction of transition metal atoms into γ'-Fe_4N can generally improve some properties of the materials,[10–12] such as magnetic properties, corrosion resistance and mechanical ductility. In this paper we report the Sn substituted for Fe in γ'-Fe_4N compounds, and mainly analyze the MVE and CBE of Sn atom. The aim is to search the scientific basis of the changed properties for the γ'-$(Fe_{1-x}Sn_x)_4N$ compounds.

2 EXPERIMENTAL

Using oxalate cooprecipitation technology, the original $(Fe_{1-x}Sn_x)C_2O_4 \cdot nH_2O$ powder were prepared. In H_2/NH_3 atmosphere, the $(Fe_{1-x}Sn_x)C_2O_4 \cdot nH_2O$ powder were heat-treated directly, then quenched at room temperature. Adjusting the heat treatment condition, the single phase γ'-$(Fe_{1-x}Sn_x)_4N$ were synthesized in the composition range $0 \le x \le 0.3$.[13] The lattice structure was measured by a D/MAX-2400 type x-ray diffraction spectrometer. The high-pressure Mössbauer measurements were performed in a Chester- Jones-Type high-pressure setup with B_4C anvils.[5,6,14] All Mössbauer spectra were recorded at room temperature with a Halder MR-351 type spectrometer. A 50 mCi $^{57}Co(Rh)$ source was used. All measured isomer shift IS are relative to that of α-Fe at room temperature.

3 RESULTS AND DISCUSSION

In Fig.1, some of the x-ray diffraction patterns of γ'-$(Fe_{1-x}Sn_x)_4N$ are given. The results indicate that all the samples are the face centered cubic structure in the composition range $0 \le x \le 0.3$, where the Fe and Sn atoms occupy the corner site (I) and the face center site (II), and the N atom is located at the body center site. With the increasing of Sn content, the diffraction peaks shift to the small angle side, which represents that the substitution of Sn atom for Fe atom causes a monotonous increase of the lattice parameter as shown in Fig.2. The experimental data of lattice parameter can be well fitted with the following two linear formulas

$$\alpha_0(x) = 3.795 + 0.019 \times x \qquad (0.0 \le x \le 0.10)$$

$$\alpha_0(x) = 3.797 + 0.228 \times (x - 0.1) \qquad (0.10 \le x \le 0.30) \qquad (1)$$

where x, in unit of 0.1 nm, is the Sn content in γ'-$(Fe_{1-x}Sn_x)_4N$.

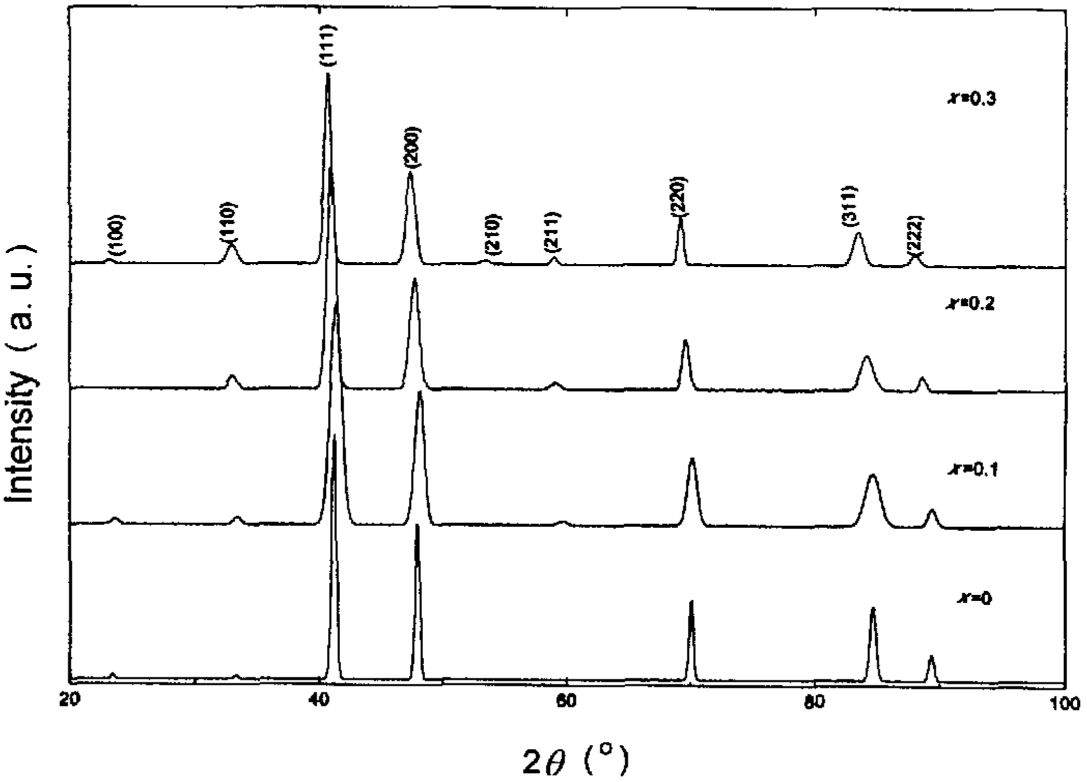

Fig.1 X-ray diffraction patterns of γ'-$(Fe_{1-x}Sn_x)_4N$

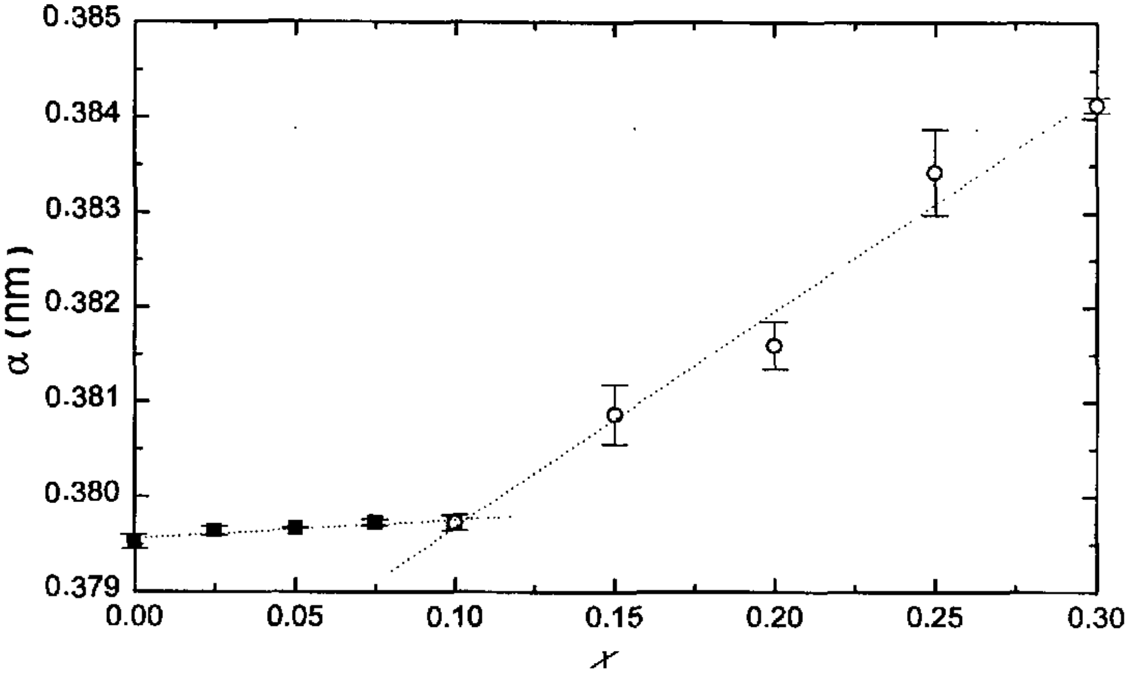

Fig.2 Composition dependence of lattice parameter of γ'-$(Fe_{1-x}Sn_x)_4N$

As mention above, the structure type of solid solution retains the same before and after the introduction of the substitutional atom, the change of the properties of the material results from the MVE and CBE of the introduced atom. For γ'-$(Fe_{1-x}Sn_x)_4N$, although the unit cell volume and the properties are different from that of γ'-Fe_4N, but their lattice structure is the same, so the difference of properties between γ'-$(Fe_{1-x}Sn_x)_4N$ and γ'-Fe_4N comes from the total contribution of Sn atom. If the unit cell volume of γ'-$(Fe_{1-x}Sn_x)_4N$ could be compressed to that of γ'-Fe_4N, the difference of properties between the compressed γ'-$(Fe_{1-x}Sn_x)_4N$ and γ'-Fe_4N should be caused only by the CBE of Sn atom. Certainly, the MVE of Sn atom can be obtained by comparing the total effect and the CBE of Sn atom.

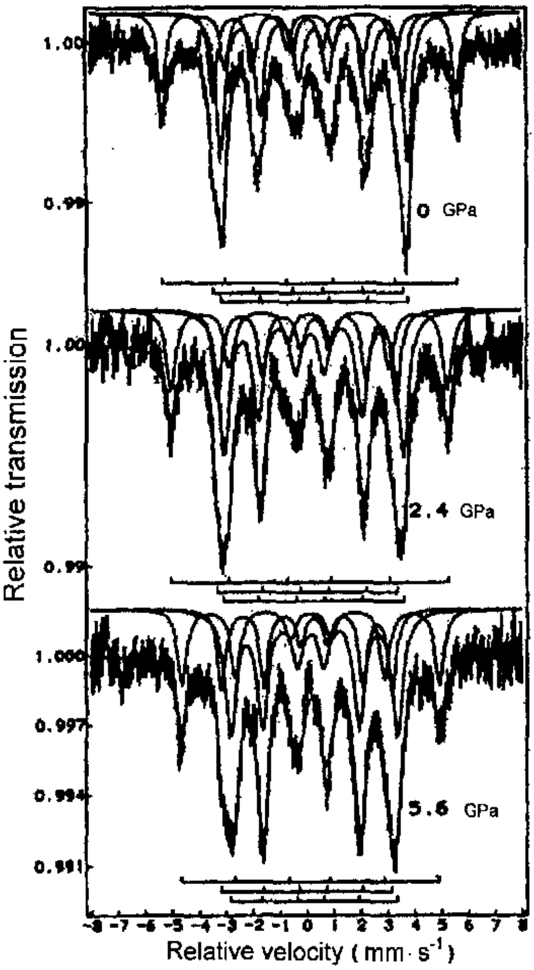

Fig.3 High-pressure Mössbauer spectra of γ'-Fe_4N at room temperature[5,6]

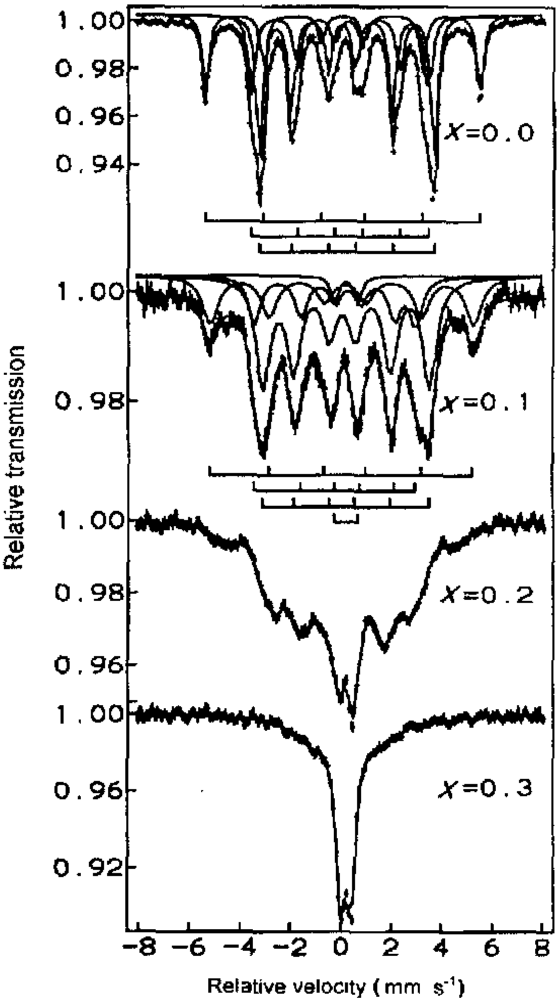

Fig.4 Mössbauer spectra of γ'-$(Fe_{1-x}Sn_x)_4N$ at room temperature

In the γ'-Fe_4N structure the iron atoms occupy two non-equivalent crystallographic sites: FeI and FeII sites. Because the easy magnetization direction of the γ'-Fe_4N is parallel to the [100] direction, the Mössbauer subspectrum of FeII site is split into two subspectra with their intensity ratio of 2:1. Therefore the Mössbauer spectra of γ'-Fe_4N compound was resolved into three sextets with relative intensities ratio 1(FeI):2(FeIIA): 1(FeIIB).[9] The high-pressure Mössbauer spectra of γ'-Fe_4N is shown in Fig.3 and the pressure dependencies of the hyperfine magnetic field $B_{\rm hf}$ and the IS of γ-Fe_4N are given in Table 1 of Ref.[6]. It is proved that the pressure dependence of the hyperfine magnetic field and the isomer shift generally satisfies the following relation[15]

$$\ln B_{\rm hf}(p) = \ln B_{\rm hf}(0) + bp$$

$$IS(p) = IS(0) + cp \tag{2}$$

where b and c are constant, p is the pressure.

It is also known that the stress of material generally satisfies the Huck's law. From the definition of compressive coefficient κ the pressure dependence of unit cell volume $V(p)$ can be expresses as following

$$\ln V(p) = \ln V(0) + \kappa p \tag{3}$$

where the value of κ is $-5.1 \times 10^{-3}\mathrm{GPa}^{-1}$ for γ'-Fe_4N.[16] Supposing γ'-$(Fe_{1-x}Sn_x)_4N$ has the same compressive coefficient with γ'-Fe_4N. Obviously, if the unit cell volume of γ'-$(Fe_{1-x}Sn_x)_4N$ can be obtained, using (3) we can firstly determine the pressure p which is needed to press γ'-$(Fe_{1-x}Sn_x)_4N$ to the same unit cell volume of γ'-Fe_4N, then we can calculate the $B_{\rm hf}$ and IS of γ'-Fe_4N at this volume using (2), so the MVE of Sn atom on the $B_{\rm hf}$ and IS can be derived. Then one can obtain the CBE of Sn atom on the $B_{\rm hf}$ and IS using the total change minus the MVE easily. Actually, the essential prerequisite has been solved by x-ray diffraction measurements.

The room temperature Mössbauer spectra of γ'-$(Fe_{1-x}Sn_x)_4N$ are given in Figure 4. After the substitution of Sn atoms for Fe, the Mössbauer spectra become complex. There are two distinct changes, one is that the line width is obviously enlarged which results from the nearest neighbor and the next nearest neighbor environment of FeI and FeII in γ'-$(Fe_{1-x}Sn_x)_4N$, the other is the change of peak shape. When $x \geq 0.1$, there added is one broadened doublet which results from the decreasing of Curie temperature due to the substitution of diamagnetism Sn atoms. In this paper, we fit the spectra with one or two broadened subspectra for each site, and add one doublet when $x \geq 0.1$. For $x=0.3$, we fit the spectra using one sextet and one doublet, so one can only get its average value of $B_{\rm hf}$ and IS. The unit cell volume dependence of hyperfine magnetic fields and isomer shifts derived from high-pressure Mössbauer measurements on Fe_4N and Mössbauer measurements on $(Fe_{1-x}Sn_x)_4N$ at room temperature are shown in Fig.5 and Fig.6. The linear fitting results are list in Table 1.

Table 1 Hyperfine parameters $B_{\rm hf}$ (Hyperfine magnetic field) and IS (Isomer Shift) changes caused by MVE and CBE of Sn atom (The linear correlation coefficient is given in parentheses)

	Total Effect	MVE	CBE	MVE/CBE
$\partial \ln B_{hf}^{\rm I}/\partial \ln V$	-6.77(0.955)	5.00(0.977)	-11.77	0.42
$\partial \ln B_{hf}^{\rm II}/\partial \ln V$	-10.18(0.986)	4.32(0.980)	-14.50	0.30
$\partial \ln B_{hf}^{\rm av}/\partial \ln V$	-13.59(0.974)	4.61(0.977)	-18.20	0.25
$\partial IS^{\rm I}/\partial \ln V$ (mm/s)	-5.16(0.97)	0.27(0.63)	-5.43	0.05
$\partial IS^{\rm II}/\partial \ln V$ (mm/s)	3.17(0.77)	1.49(0.96)	1.68	0.89
$\partial IS^{\rm av}/\partial \ln V$ (mm/s)	2.50(0.75)	1.15(0.86)	1.35	0.85

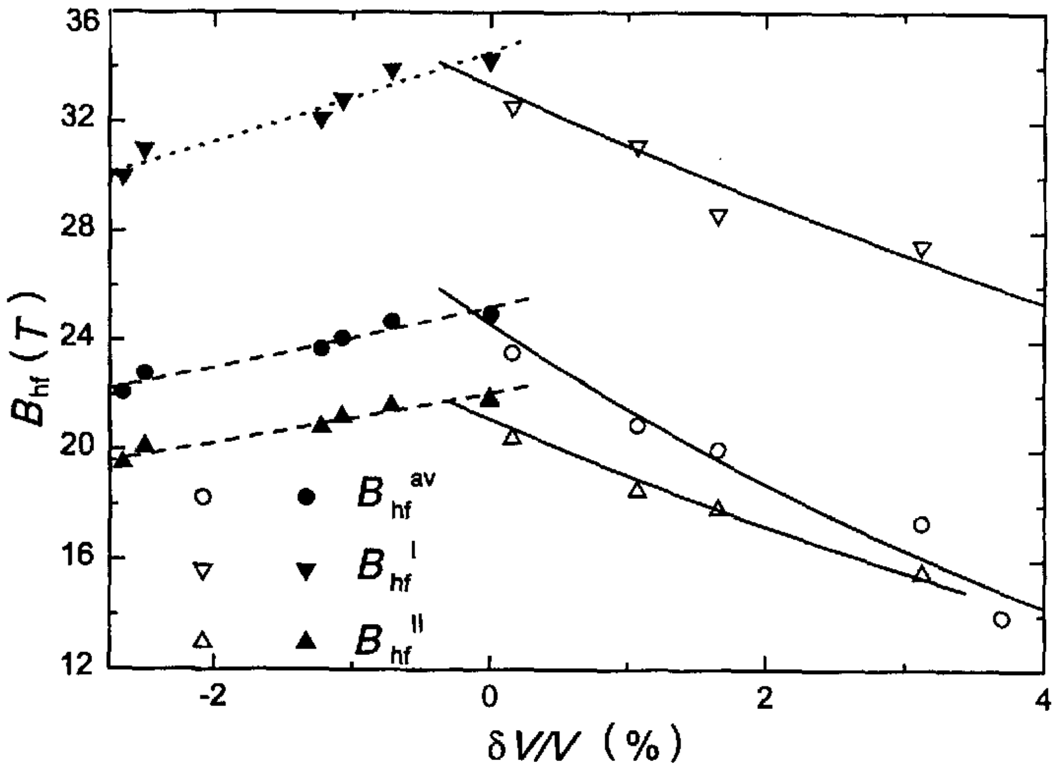

Fig.5 Unit cell volume dependence of the hyperfine fields derived from high-pressure Mössbauer measurements on Fe_4N at room temperature (solid symbols) and from room temperature *Mössbauer measurements on* $(Fe_{1-x}Sn_x)_4N$ *(open symbols)*

The contribution of the MVE and CBE of Sn atom to the $B_{\rm hf}$ can be obtained from Fig.5. $B_{\rm hf}^{\rm I}$, $B_{\rm hf}^{\rm II}$ and $B_{\rm hf}^{\rm av}$ stand for the hyperfine field of FeI atom, FeII atom and the weighted average value for all subsextets, respectively. It is found that the MVE is a positive effect for site I, II and average field. With increasing Sn content, the expansion of unit cell volume of γ'-$(Fe_{1-x}Sn_x)_4N$ will increase the hyperfine magnetic field at site I and II, and the relation between the composition and $B_{\rm hf}$, which is affected by the lattice parameter, is linear. This is because the increasing of unit cell volume causes an increase of the difference of energy band between spin-up and spin-down $3d$ electrons of iron.[17]

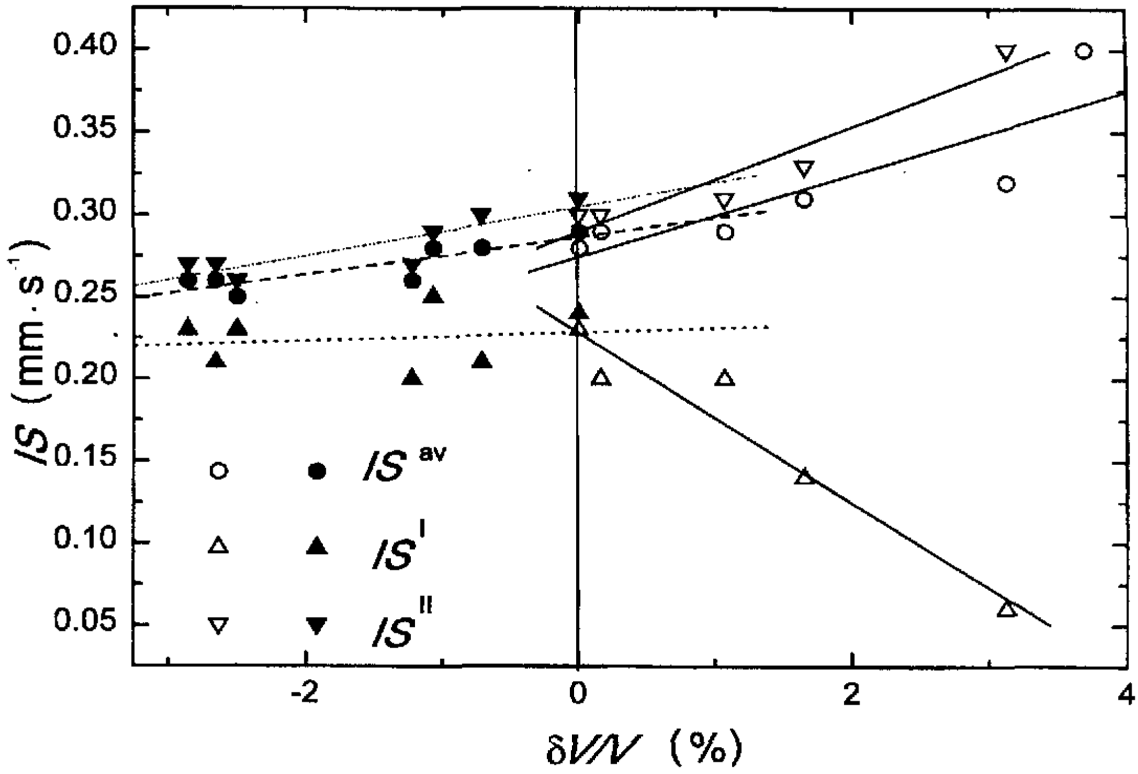

Fig.6 Unit cell volume dependence of the isomer shifts derived from high-pressure Mössbauer measurements on Fe_4N at room temperature (solid symbols) and from room temperature Mössbauer measurements on $(Fe_{1-x}Sn_x)_4N$ (open symbols)

The contribution of the CBE of Sn atom is a negative effect, and their composition dependence is linear, also. The increasing of unit cell volume will increase the distance of Fe–N and FeI–FeII, which will abate interaction between them. As a consequence, the substitutional Sn atom to Fe would decrease the hyperfine field of Fe atoms because the Sn atom is anti-paramagnetic. From Table 1, you can see that the contribution of the CBE of Sn atom to B_{hf} is predominant, the contribution of MVE is only 25%–42% that of CBE. So the CBE plays a principal role in the change of the hyperfine magnetic field in γ'-$(Fe_{1-x}Sn_x)_4N$.

The influence of the MVE and CBE of Sn atom on the isomer shift can be obtained from Fig.6, and the linear fitting results are also listed in Table 1. IS^{I}, IS^{II} and IS^{av} stand for isomer shift of FeI atom, FeII atom and the weighted average value, respectively. It is found that the contribution of MVE and CBE to site II and CBE to site I is positive, but that of MVE to site I is negative.

The MVE is a positive effect, and it increases monotonously with the increasing of Sn content. It is known that the isomer shift is mainly determined by the concentration of s electron at nuclear site. With increasing x, the unit cell volume increases, this means the 4s electron cloud is expansion, which makes an increase of the isomer shift, so this part gives a positive contribution to the MVE for both site I and II.

As mentioned above, with the increasing of tin concentration, the distance of FeI–FeII and FeII–N increases, the interaction between FeII atoms and N or FeI weakens. As both FeI and N atoms act as the donor of electrons, the FeII atoms are the only acceptor of electrons[5] in Fe_4N-like compounds. So it will decrease the density of 4s-like electron charge of FeI nuclei and increase the density of 4s-like electron charge of FeII nuclei. As a consequence, with the increasing of Sn, the *IS* on site I decreases and that on site II increases. Therefore the contribution of CBE on sites I and II are different.

Just as the hyperfine magnetic field, the influence of the CBE of Sn on the isomer shift is the chief effect for either site I or site II obviously.

In conclusion, we have studied the structure and the hyperfine interaction of Sn substituted for Fe in γ'-Fe_4N by using the x-ray diffraction and the Mössbauer spectra. The results of x-ray diffraction indicate that single phase γ'-$(Fe_{1-x}Sn_x)_4N$ can be formed in the composition range $0 \leq x \leq 0.3$, and with the increasing of Sn content the lattice parameter can be well fitted with two linear relation. The influence of the MVE and CBE of Sn atom on B_{hf} and *IS* of Fe were distinguished. And the result indicates that the CBE plays a main role in the change of properties of γ'-$(Fe_{1-x}Sn_x)_4N$.

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