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Electronic structures and magnetism of $LaNi_{5-x}Fe_x$ compounds

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A systematic study of the magnetic moments and hyperfine interactions of the $LaNi_{5-x}Fe_x$ compounds was performed using the spin-polarized tight-binding-linear-muffin-tin-orbital methods (TBLMTO). The calculated results were compared with neutron diffraction and Mössbauer experimental data and found to be in good agreement. Fe atoms exhibit more localized magnetic moments in $LaNi_{5-x}Fe_x$ when the Fe content x is lower than 1.0. The calculated magnetic moments of the Fe atoms approach values as large as $2.5\mu_B$ due to the dilution effect. The strong $s-d$ hybridization between the Ni and La atoms and the neighboring Fe in the Fe-substituted samples results in a large transferred valence contribution to the total hyperfine field. It is found that the Fe and Ni magnetic moments decrease abruptly at a unit cell volume which is 5% smaller than the observed volume in $LaNi_4Fe$ due to the instability of the Fe magnetic moment. $LaNi_5$ becomes ferromagnetic when the unit cell volume is larger than its original volume. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1357854]

The investigation of rare earth-transition metal intermetallic compounds has been the subject of many fundamental and technological studies. Current interest in the electronic properties of $LaNi_5$ is due to its high capacity for hydrogen absorption[1] and its strong exchange-enhanced Pauli paramagnetism.[2] The $LaFe_5$ intermetallics do not exist; however, solid solutions exist for $LaNi_{5-x}Fe_x$ $(0<x<2.0)$.[3–8] $LaNi_{5-x}Fe_x$ possesses the hexagonal $CaCu_5$ structure (space group P6/mmm) with one formula unit per unit cell. This crystal structure is extremely simple, with Ni atoms occupying two different crystallographic sites, $3g$ and $2c$, Fe preferably occupying $3g$ sites and La occupying the $1a$ sites. $La(Ni, Fe)_5$ shows some interesting features of magnetic properties such as spin glass behavior which has been observed at low temperature for compounds with small amounts of Ni substituted by Fe.[6,7] The Fe atoms carry a local magnetic moment of $1.2-1.5\mu_B$ which is deduced from Mössbauer experiments.[4] This value is much smaller than the theoretical value of $2.2\mu_B$/Fe. The relationship between the electronic structure and magnetic properties of this compound has not been fully understood.

In this article, we present self-consistent spin-polarized linear-muffin-tin orbital (LMTO) band calculations for $LaNi_{5-x}Fe_x$. Based on the results of the spin-polarization calculation, the magnetic moments and hyperfine fields have been obtained and compared with experimental results.

The self-consistent tight-binding (TB) LMTO atomic-sphere-approximation method has been employed to perform a scalar relativistic band calculation. This method has been described in detail elsewhere.[9,10] In our calculation, the exchange and correlation term takes the form deduced by Von Barth and Hedin.[11] The *s*, *p*, and *d* orbitals are used for Fe and Ni, and *s*, *p*, *d*, *f* orbitals are used for La atoms. The atoms sphere radii are chosen using an automatic procedure developed by Krier *et al.*[12] The calculation is performed for 512 k points in the irreducible parts of the Brillouin zone. The atomic positions of $LaNi_{5-x}Fe_x$ are scaled according to experimental results.[3] Convergence is assumed when the root-mean-square error of the self-consistent total energy is smaller than 10^{-6} Ry. We have performed calculations for $LaNi_{5-x}Fe_x$ ($x=0.5$, 1.0, 1.5, 2.0, and 3.0). Supercells with $La_2Fe_7Ni_3$ and La_2Ni_9Fe have been used for $x=0.5$ and 1.5 compounds. For $x=2.0$ and 3.0 compounds, due to the fact that experimental parameters are not available, we have linearly extrapolated the experimental data, and obtained lattice parameters of $a=5.081$ Å, $c=4.049$ Å, $a=5.202$ Å, and $c=4.0974$ Å. The calculations are also performed for $LaNi_5$ and $LaNi_4Fe$ with various unit cell volumes, so that the dependence of the magnetic properties and total energies on the volumes is determined. The hyperfine fields H_{FC} of $LaNi_{5-x}Fe_x$ are calculated according to the prescription given by Akai *et al.* for scalar-relativistic calculations.[13]

The total density of states (DOS) for $LaNi_{5-x}Fe_x$ ($x=0.0$, 1.0, 2.0, and 3.0) and the DOS of Fe atoms are presented in Fig. 1. $LaNi_5$ is paramagnetic and the Fermi level lies near the minimum of the total DOS. After Fe substitution, the total DOS of all compounds show exchange splitting, and the Fermi level lies above the spin up DOS. As expected, the *d* states dominate the DOS of the Fe and Ni atoms, as well as the total DOS near the Fermi energy. The DOS of La atoms lie above Fermi level. The spin down DOS of Fe consists of one peak for the $x=1.0$ compound, but a continuous region is formed as the Fe content increases due to the strong interactions between Fe–Fe, Fe–Ni, and Fe–La. The calculated magnetic moments and the hyperfine fields of Fe atoms are shown in Figs. 2 and 3. As a comparison, we have included some available experimental results in these two figures. The calculated results of magnetic moments and hyperfine fields are in good agreement with the our experimental results and the results of Ref. 4. Fe atoms possess a magnetic moment as large as $2.5\mu_B$, which is due to a very large exchange splitting and exhibits a strong fer-

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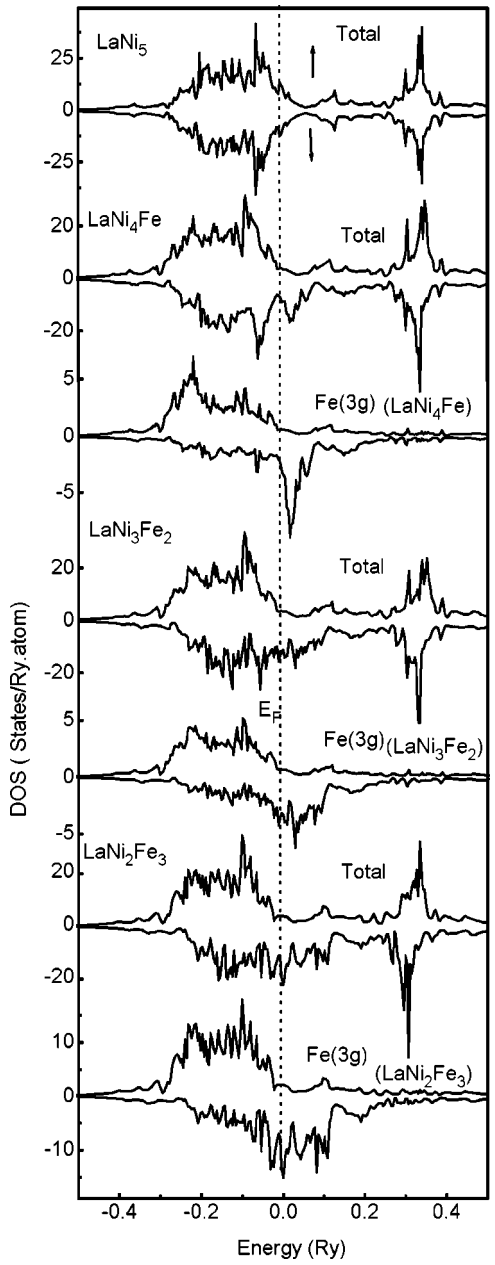

FIG. 1. Total densities of states of $LaNi_{5-x}Fe_x$ ($x=0.0$, 1.0, 2.0, and 3.0) and Fe atoms (the label in the parentheses is the corresponding compound).

romagnetism. Since $LaNi_5$ is paramagnetic, due to the dilution effect, Fe atoms tend to form a narrow *d* band when the Fe concentration is low. The Ni atoms have magnetic moments in the range of $0.2-0.5\mu_B$. The magnetic moments of the Ni atoms increase with Fe content due to the enhanced interaction between Fe and Ni atoms. The La atoms have negative magnetic moments which are induced by the Fe atoms.

Furthermore, the hyperfine fields can provide more details of the electron interactions in these compounds. We can decompose the Fermi contact field H_{FC} into two parts; H_{FC}^{core}, which is the contribution of the core electrons and comes from the polarization of the core by the polarized *d* electrons, and H_{FC}^{val}, which comes from the polarization of the valence electrons. The H_{FC}^{core} and H_{FC}^{val} contributions to H_{FC} are also

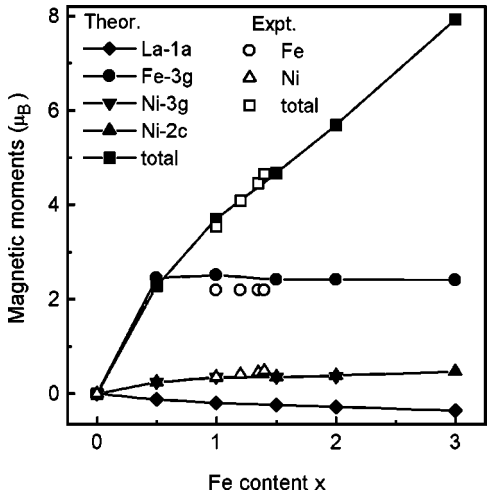

FIG. 2. The calculated magnetic moments of different atoms in $LaNi_{5-x}Fe_x$ and total magnetic moments in a unit cell. The hollow symbol represents the experimental values which were measured in a magnetic field of 5 T using a superconducting quantum interference device at 30 K.

shown in Fig. 3. It can be seen that the H_{FC}^{core} at the Fe sites is a dominant contribution to the H_{FC}. The H_{FC}^{val} has an opposite sign to the core contribution and has a value of 10 T which is much higher than that of α-Fe(-5 T). This feature is quite different from most of the R–Fe intermetallics where both core and valence contribution are of the same sign. From Fig. 3, very large values of H_{FC}^{val} were obtained, suggesting that a strong $s-d$ hybridization between Fe atoms and other atoms occur, and it decreases with increasing Fe content because of decreasing number of the Ni atoms in the unit cell. Thus, the $s-d$ hybridization is very important in the $La(Ni, Fe)_5$ compounds, especially when Ni is substituted by a small amount of Fe($x \leqslant 1.0$) (The absolute value of the valence hyperfine field is nearly half of the total hyperfine field).

The dependence of H_{FC}, H_{FC}^{core}, and H_{FC}^{val} on the magnetic moments (μ_{Fe}) at the Fe sites is shown in Fig. 4. A linear relationship between the H_{FC}^{core} and local magnetic mo-

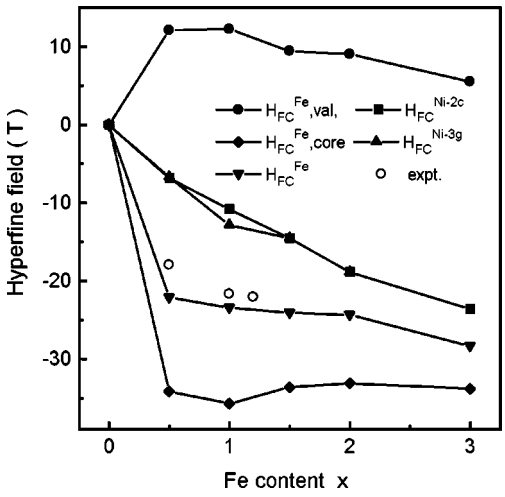

FIG. 3. The calculated hyperfine fields of different atoms in $LaNi_{5-x}Fe_x$. The hollow circles represent the experimental hyperfine fields which are taken from Ref. 4.

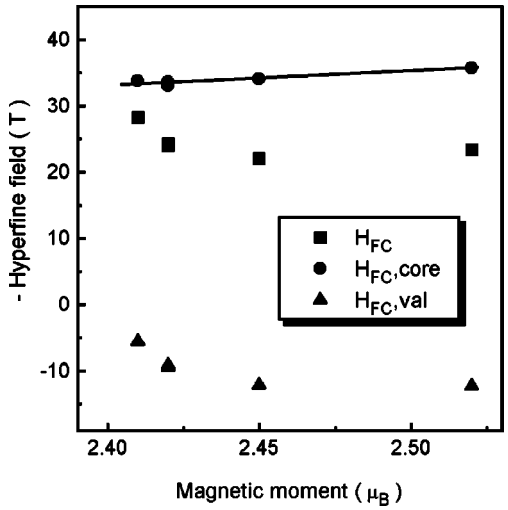

FIG. 4. The dependence of H_{FC}^{core} and H_{FC}^{val} at the Fe($3g$) sites on Fe magnetic moments (μFe) in $LaNi_{5-x}Fe_x$.

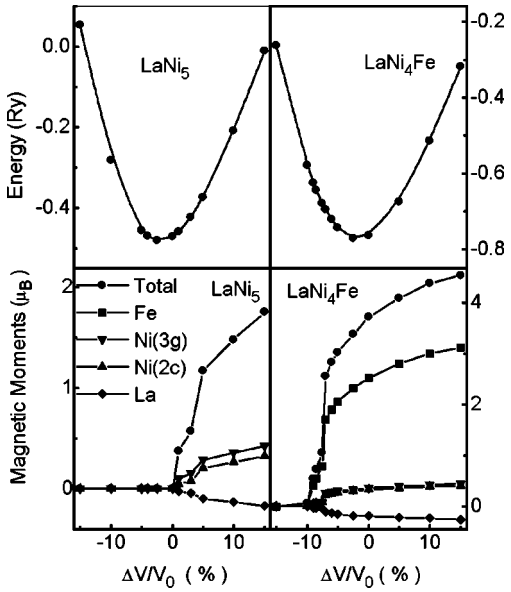

FIG. 5. The magnetic moments and total energy dependence on the unit cell volumes of $LaNi_{5-x}Fe_x$ ($x=0.0,1.0$) (V_0 is the observed volume).

ments is observed, and the proportional coefficient is estimated to be about $-15\,\text{T}/\mu_B$, whereas the valence contribution and total hyperfine field are not proportional to the magnetic moments of the Fe atoms. This is the reason why the magnetic moments obtained from Mössbauer measurements in Ref. 4 are much lower than the magnetic measurements data, though the transfer factor ($14.5\,\text{T}/\mu_B$) is almost the same as our calculated results ($15\,\text{T}/\mu_B$). Hence, it can be seen that the H_{FC} at the Fe sites is affected by two factors, μ_{Fe} and the polarization of the valence electrons.

Figure 5 is the dependence of the magnetic moments and total energies on the unit cell volumes of $LaNi_5$ and $LaNi_4Fe$. The minimum total energy is achieved when the unit cell is about 2.5% smaller than the observed volume V_0 for $LaNi_5$ and $LaNi_4Fe$. At the observed unit cell volume V_0, $LaNi_5$ is paramagnetic. The Ni and La atoms will possess magnetic moments when the unit cell volume of $LaNi_5$ is increased. A sharp increase of the magnetic moment of the Ni atoms is observed at an expansion rate of $\Delta V/V_0=5\%$. The magnetic moments increase monotonously when $\Delta V/V_0>5\%$. Therefore, $LaNi_5$ may become ferromagnetic with increasing unit cell volume. The magnetic moment of $LaNi_4Fe$ shows an abrupt decrease when the $\Delta V/V_0=-5\%$, and it reaches nearly zero at the critical volume $\Delta V/V_0=-10\%$ where the ferromagnetism disappears. In the range where the expansion rate $\Delta V/V_0=0\%-15\%$, the magnetic moments increase linearly. The abrupt decrease of the Fe and Ni magnetic moments in $LaNi_4Fe$ is due to the instability of the Fe magnetic moments. These results show that the Fe and Ni atoms might lose their magnetic moments under high pressure in $LaNi_4Fe$.

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[1] In *Hydrogen in Metals*, Vols. 1 and 2, edited by G. Alefeld and J. Völk (Springer, Berlin, 1978).
[2] D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. **135A**, 1356 (1964).
[3] C. Y. Tai, C. Tan, G. K. Marasinghe, O. A. Pringle, W. J. James, M. Chen, W. B. Yelon, J. Gebhardt, and N. Ali, IEEE Trans. Magn. **35**, 3346 (1999).
[4] J. Lamloumi, A. Percheron-Guegan, J. A. Achard, G. Jehanno, and D. Givord, J. Phys. (France) **45**, 1643 (1984).
[5] M. Gerlach, N. Mommer, M. Hirscher, and H. Kronmüller, J. Alloys Compd. **267**, 47 (1998).
[6] M. Escorne, J. Lamloumi, A. Percheron-Guegan, J. A. Achard, A. Mauger, and G. Jehanno, J. Appl. Phys. **45**, 4121 (1988).
[7] M. Escorne, A. Mauger, J. Lamloumi, and A. Percheron-Guegan, Solid State Commun. **89**, 761 (1994).
[8] S. J. Campbell, R. K. Day, J. B. Dunlop, and A. M. Stewart, J. Magn. Magn. Mater. **31–34**, 167 (1983).
[9] O. K. Anderson and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
[10] O. K. Anderson, Z. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986).
[11] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[12] G. Krier, O. K. Anderson, and O. Jepsen (unpublished).
[13] H. Akai, M. Akai, S. Blügel, B. Drittler, E. Ebert, K. Terakura, R. Zeller, and P. H. Dederichs, Prog. Theor. Phys. Suppl. **101**, 11 (1990).