Journal of Alloys and Compounds, 190 (1992) 73–76
JALCOM 403

Mössbauer effect study on magnetic properties of intermetallic compounds $(Sm_{1-x}Y_x)_2Fe_{17}N_y$

Zeng Yiwei and Luo Guangsheng
Department of Physics, Beijing Normal University, Beijing 100875 (China)

Lu Yi, Tang Ning and Yang Fuming
Magnetism Laboratory, Institute of Physics, Academia Sinica, PO Box 603, Beijing 100080 (China)

(Received April 1, 1992; in final form June 29, 1992)

Abstract

Mössbauer spectroscopy was used to study the substitution effect of Y for Sm atoms and the occupation of N atoms in $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0; $2<y<3$). Our results show that the N atoms in these nitrides occupy not only *9e* sites but also *3b* sites. The experimental results have confirmed the following facts. (1) The crystal structure changes when x exceeds 0.5. (2) The average magnetic hyperfine fields at the different iron sites in $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ vary with the yttrium concentration. (c) $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ compounds display an easy *c* axis anisotropy as the yttrium content ranges from $x=0$ to 0.8 according to the Mössbauer fitting results.

---

1. Introduction

A new series of high performance permanent magnet materials $R_2Fe_{17}N_y$ was discovered in 1990 [1]. This is one of the most important developments recently in the field of magnetism and magnetic materials. The results obtained show that remarkable improvements in magnetic properties can be achieved by introducing nitrogen into the binary alloys R_2Fe_{17}. In particular, the Curie temperature and saturation magnetization have markedly improved. However, some features of the micromechanism of the effect of nitrogen on improving the magnetic properties of the binary compounds R_2Fe_{17} are still not clear. For instance, it is not known whether N atoms occupy only one site inside the host matrix [2] or why none of these compounds display an easy *c* axis anisotropy over the range of the rare earth series except for samarium. It is also insufficiently known how to prepare the rare earth iron nitrides without any impurity phases, especially the α-Fe phase.

In this work we have investigated several fundamental aspects of the $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ compounds ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0; $2<y<3$) using Mössbauer spectroscopy. These aspects are: (1) the occupation of interstitial sites by N atoms; (2) the influence of substitution of Y for Sm atoms on the micromechanism of the magnetic properties; (3) the reason why the $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ compounds retain an easy *c* axis anisotropy as the yttrium content varies over a large range, *i.e.* from $x=0$ to 0.8. These aspects are clearly important for understanding how nitrogen improves the magnetic properties of these newly discovered permanent magnetic materials.

2. Experimental details

Samples of $(Sm_{1-x}Y_x)_2Fe_{17}$ with $x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0 were prepared by arc melting appropriate quantities of the elements. The ingots obtained by arc melting were annealed in a high vacuum at 1373 K for 4 h. Then the samples were pulverized in 1 atm N_2 gas at about 723 K for 2 h to obtain the nitrides $(Sm_{1-x}Y_x)_2Fe_{17}N_y$. The nitrogen content was determined by weighing to be in the range $2<y<3$. X-ray diffraction with Cu Kα radiation was used to determine the crystal structure, phase composition and lattice parameters.

The ^{57}Fe Mössbauer absorption spectra were collected at room temperature for Sm_2Fe_{17} and $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0) using a conventional constant-acceleration MS-500 spectrometer with a ^{57}Co–Pd source. The velocity scale was calibrated using an α-Fe foil absorber of thickness 25 μm at room temperature. Samples consisted of about 15 mg cm^{-2} $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ powder mixed with sugar to form homogeneous and isotropic absorbers. All the Mössbauer spectra data were analysed by the MOSFUN least-squares method and were fitted with seven in-

0925-8388/92/$5.00

dependent lorentzian sextets whose intensity ratios were constrained as 2:1:2:2:4:2:4 for the 6*c*(4*f*), 9*d*$_1$(6*g*$_1$), 9*d*$_2$(6*g*$_2$), 18*f*$_1$(12*j*$_1$), 18*f*$_2$(12*j*$_2$), 18*h*$_1$(12*k*$_1$) and 18*h*$_2$(12*k*$_2$) iron sites respectively, one sextet for the α-Fe phase and one doublet for the paramagnetic phase.

3. Results and discussion

Analysis by X-ray diffraction showed that the samples with $x<0.5$ have the rhombohedral Th_2Zn_{17}-type structure while those with $x>0.5$ have the hexagonal Th_2Ni_{17}-type structure. It was also found that there were small amounts of α-Fe in the samples. Analysis of the Mössbauer spectra of Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$ displayed in Fig. 1 indicates about 2% α-Fe and 6% paramagnetic phase in Sm_2Fe_{17}. The main phase in Sm_2Fe_{17} is present to about 92%, but the α-Fe phase increases dramatically after nitrogenation, reaching about 17%. However, the relative amount of the paramagnetic phase is basically unchanged for the various compounds. The isomer shift (IS) relative to α-Fe and the electric quadrupole splitting (QS) for the paramagnetic phase are about 0.30 mm s^{-1} and 0.98 mm s^{-1} respectively. The results of the fitting using subspectra corresponding to the different iron sites of Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$ are listed in Table 1 (*B* is the magnetic hyperfine field).

The magnetic hyperfine fields given in Table 1 agree with the results of Hu and co-workers [3, 4]. By considering the different angles between the magnetization direction and the principal axis of the electric field gradient and the contribution of the dipolar field, we fitted all the Mössbauer spectra with seven sextets for four different iron sites and constrained their intensity ratios as mentioned above in accordance with the results of Hu *et al.* [4]. It is necessary to explain that the magnetization direction, regardless of whether it is parallel or perpendicular to the *c* axis, on fitting the Mössbauer spectra, influences the subspectra of all iron sites except the 6*c*(4*f*) site. This influence leads to a splitting into two or three groups with different intensity ratios for the Th_2Zn_{17}-type and Th_2Ni_{17}-type structures. The main difference between the Th_2Zn_{17}-type and Th_2Ni_{17}-type structures is at the 12*j* site, which should split into three groups with an intensity ratio of 1:1:1. Since the dipolar fields at two of the three groups of the 12*j* sites in Th_2Ni_{17}-type compounds are very close, we treat them in the same way as Hu *et al.* [4] did.

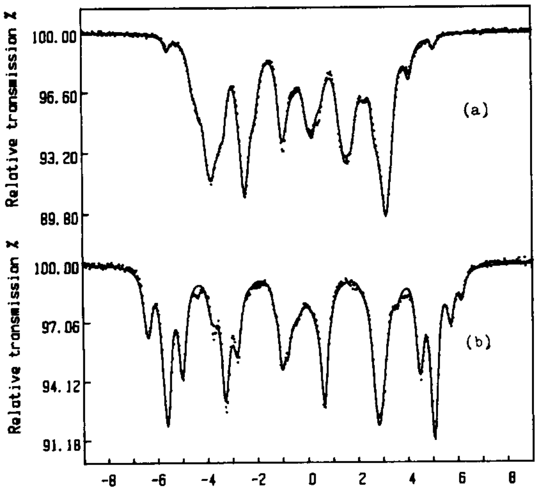

Fig. 1. Mössbauer spectra of (a) Sm_2Fe_{17} and (b) $Sm_2Fe_{17}N_y$.

It is noteworthy that not only the values but also the signs of the electric quadrupole splitting for the 18*f* and 18*h* sites have changed after nitrogenation. The variation in QS for the 18*f* and 18*h* sites is about 0.38 and 0.21 mm s^{-1} respectively. This may be taken as an evidence that the N atoms occupy another interstitial site in addition to the 9*e* site [5]. On the basis of ref. 5, if the *N* atoms only occupy the 9*e* sites, then the QS values of the 18*f* and 18*h* sites are expected to shift in the positive velocity direction. This result disagrees with the results of Ibberson *et al.* [6], which indicate a strong preference for exclusive single-site occupation of the N atoms at the 9*e* position of the rhombohedral compound $Nd_2Fe_{17}N_y$, but supports the conclusion of Jaswal *et al.* [7].

When the Sm atoms of Sm_2Fe_{17} and its nitrides are partly replaced by Y atoms, the crystal structure changes from the Th_2Zn_{17} type to the Th_2Ni_{17} type for $x>0.4$. This is confirmed by the results of Mössbauer spectra fitting given in Fig. 2 and Table 2. It can be seen from Table 2 that the yttrium concentration dependence of the magnetic hyperfine fields at different iron sites of $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ compounds is different. The values of the magnetic hyperfine field for the 6*c* and 9*e* sites decrease with increasing yttrium content, but no obvious variation is observed at the 18*f* and 18*h* sites as the yttrium content increases. This experimental result reveals that the Y atoms preferentially occupy the 2*b* sites. According to the theoretical calculation of Jaswal *et al.* [7], one can expect a reduction in the iron moment for those atoms with nitrogen nearest neighbours. It is well known that the R atoms occupy two sites, *i.e.* the 2*b* and 2*d* sites, in $R_2Fe_{17}N_y$ compounds. Since the Sm atoms at the 2*b* sites are first replaced by Y atoms, this leads to a reduction in the magnetic hyperfine fields at the 6*c* and 9*d* sites.

Substitution of Y atoms for Sm atoms does not only affect the relative amount of α-Fe phase in $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ samples because of the different electronegativities of Sm, Y and N atoms. It is easy to infer from the data that the proportion of α-Fe phase decreases with increasing yttrium content (see Fig. 3) except for $x=1.0$, but the nearest-neighbour coordinations for the different iron sites are also changed,

TABLE 1. Results of the fitting of the Mössbauer spectra of Sm_2Fe_{17} and $Sm_2Fe_{17}N_y$

Compound	Site 6*c*			Site 9*d*			Site 18*f*			Site 18*h*		
	IS (mm s^{-1})	QS (mm s^{-1})	*B* (T)	IS (mm s^{-1})	QS (mm s^{-1})	*B* (T)	IS (mm s^{-1})	QS (mm s^{-1})	*B* (T)	IS (mm s^{-1})	QS (mm s^{-1})	*B* (T)
Sm_2Fe_{17}	0.046	−0.18	26.8	−0.11	−0.052	22.9	−0.15	0.23	21.2	−0.072	0.023	19.6
$Sm_2Fe_{17}N_y$	0.13	−0.10	39.2	−0.078	0.014	37.3	0.011	−0.16	33.3	0.083	−0.19	29.4

TABLE 2. Mössbauer parameters of $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ for different iron sites at room temperature

Site	Parameter	Yttrium content *x*					
		0	0.2	0.4	0.6	0.8	1.0
6*c*	IS (mm s^{-1})	0.13	0.14	0.10	0.12	0.04	−0.10
	QS (mm s^{-1})	−0.10	−0.084	−0.24	−0.11	0.32	−0.34
	B (T)	39.2	39.1	38.4	38.1	37.6	36.8
9*d*	IS (mm s^{-1})	−0.078	−0.018	−0.003	−0.022	0.042	0.053
	QS (mm s^{-1})	−0.078	−0.085	−0.083	0.11	0.31	0.053
	B (T)	37.4	37.4	36.9	36.7	36.1	34.4
18*f*	IS (mm s^{-1})	0.011	0.08	0.011	−0.010	0.035	0.073
	QS (mm s^{-1})	−0.17	−0.14	0.15	0.12	0.13	−0.14
	B (T)	33.3	33.4	33.1	33.0	32.6	32.0
18*h*	IS (mm s^{-1})	0.085	0.078	0.075	0.080	0.064	0.011
	QS (mm s^{-1})	−0.20	−0.20	0.17	0.17	0.10	−0.10
	B (T)	29.4	29.6	29.5	29.5	29.7	29.0

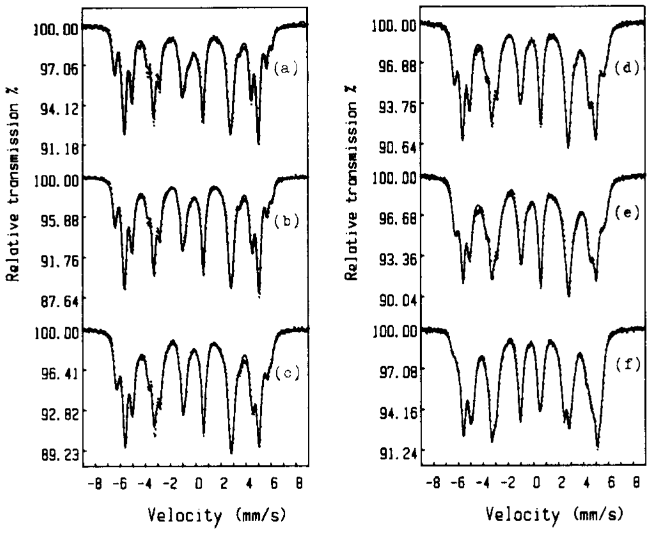

Fig. 2. Mössbauer spectra of $(Sm_{1-x}Y_x)_2Fe_{17}N_y$ compounds with (a) $x=0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$ and (f) $x=1.0$.

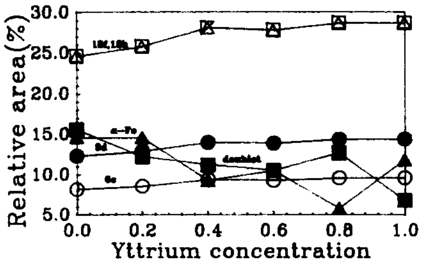

Fig. 3. Concentration dependence (x) of the relative subspectrum intensity for the different iron sites and the impurity phases in $(Sm_{1-x}Y_x)_2Fe_{17}N_y$.

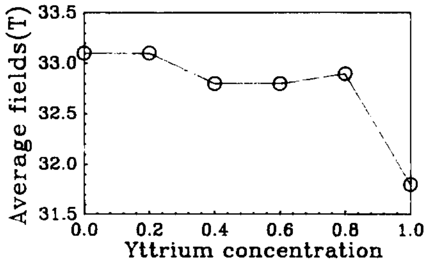

Fig. 4. Concentration dependence (x) of the average hyperfine fields in $(Sm_{1-x}Y_x)_2Fe_{17}N_y$.

since the radius of the Y atom is less than that of the Sm atom. This can change the R–Fe exchange interaction which is in competition with Fe–Fe exchange. This variation in the coordination environment of iron nearest neighbours causes the average magnetic hyperfine fields to change with yttrium concentration. The concentration dependence of the average hyperfine field is illustrated in Fig. 4. This result is consistent with results of magnetic measurements [8].

By studying Table 2 in detail, we can state the following facts. (1) The values of IS and QS at different iron sites display a sudden change with yttrium content at $x=0.6$, where the crystal structure changes from the Th_2Zn_{17} type to the Th_2Ni_{17} type. (2) For an yttrium concentration between $x=0.8$ and 1.0 the sign of QS at the 18*h* sites suddenly changes. This suggests that the easy magnetization might change from easy *c* axis to easy plane over this small range.

Acknowledgments

We wish to thank Professor Zhang Shougong for his friendly and enthusiastic help and Dr. Bo-Ping Hu for helpful discussions.

References

1 J. M. D. Coey and Hong Sun, *J. Magn. Magn. Mater., 87* (1990) L251.

2 O. Isnard, S. Miraglia, J. L. Soubeyroux, D. Fruchart and A. Stergiou, *J. Less-Common Met., 162* (1990) 273.

3 B.-P. Hu and J. M. D. Coey, *J. Less-Common Met., 171* (1991) 33.

4 B.-P. Hu, H.-S. Li, Hong Sun and J. M. D. Coey, *J. Phys.: Condens. Matter, 3* (1991) 3983.

5 K. Takahashi, Y. Ujihira, K. Kobayashi, T. Iriyama and T. Konishi, *Hyperfine Interact., 68* (1991) 413.

6 R. M. Ibberson, O. Moze, T. H. Jacobs and K. H. J. Buschow, *J. Phys.: Condens. Matter, 3* (1991) 1219.

7 S. S. Jaswal, W. B. Yelon, G. C. Hadjipanayis, Y. Z. Wang and D. J. Sellmyer, *Phys. Rev. Lett., 67* (1991) 644.

8 Y. Lu, O. Tegus Q. A. Li, N. Tang, M. J. Yu, R. W. Zhao, J. P. Kuang, F. M. Yang, G. F. Zhou, X. Li and F. R. de Boer, *Physica B., 177* (1992) 243.