Journal of Alloys and Compounds, 191 (1993) 301–304
JALCOM 526

Influence of interstitial C atoms on the Curie temperature and exchange interaction of $R_2Fe_{17}C_y$

Lin-shu Kong, Lei Cao and Bao-gen Shen
State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080 (China)

(Received September 9, 1992)

Abstract

The $R_2Fe_{17}C_y$ ($R \equiv Y$, Gd, Tb, Dy, Ho and Er; $y = 1.5$, 2.0 and 2.5) carbides were prepared by melt-spinning and found to crystallize in the hexagonal Th_2Ni_{17}-type or rhombohedral Th_2Zn_{17}-type structure. The unit cell volumes and Curie temperatures increase with the carbon content. The exchange interactions in $R_2Fe_{17}C_y$ were investigated using the molecular field model. The results indicate that the interstitial carbon atoms lead to an increase in the Fe–Fe interaction and have little influence on the R–Fe interaction. It has been shown that the enhancement of the Fe–Fe interaction is mainly caused by the volume expansion.

1. Introduction

Since the discovery of $Nd_2Fe_{14}B$, the search for novel permanent magnet materials has been concentrated on the rare earth–iron intermetallic compounds. Recently, a new series of interstitial compounds $R_2Fe_{17}X_y$ ($R \equiv$ rare earths; $X \equiv N$ or C) [1–4] have been exploited as potential candidates for high performance permanent magnets. It has been found that the interstitial atoms lead to a large increase in Curie temperature and a strong improvement of the magnetocrystalline anisotropy. Thus $R_2Fe_{17}X_y$ compounds possess excellent intrinsic magnetic properties [5], which are comparable with or surpass those of $Nd_2Fe_{14}B$. The effect of interstitial atoms on the rare earth sublattice crystal field interaction has been satisfactorily explained [6, 7], but the effect on the exchange interactions is still not well understood. It has been shown that there is a linear relationship between the Curie temperature and the corresponding unit cell volume [8, 9]. However, the $R_2Fe_{17}X_y$ compounds with $y = 1.5$–2.5 have not been investigated in detail because the interstitial atom content is limited to $y = 1.5$ for the carbides by arc melting [10] and is not well controlled by a gas-phase interstitial modification. In previous work [11, 12], we obtained the $R_2Fe_{17}C_y$ compounds with a maximum carbon content y close to 3.0 by melt spinning. Here, we report the results of unit cell volumes and Curie temperatures for $R_2Fe_{17}C_y$ with $y = 1.0$, 1.5, 2.0 and 2.5, and discuss the exchange interactions of these compounds.

2. Experimental details

The samples were prepared by arc melting the appropriate amounts of rare earth, Fe–C alloys and iron in a high purity argon atmosphere. For homogenization the samples were melted several times. The ingots were then melt spun in a high purity argon atmosphere. The quenching rate was varied by rotating the polished copper wheel with a surface velocity V_s of 0–47 m s^{-1}. The ribbons were about 1 mm wide and 20–30 μm thick. X-ray diffraction experiments were performed to determine the crystallographic structure. In addition to the X-ray patterns, thermomagnetic analysis was used to identify the single phase. The Curie temperatures were determined from magnetization *vs.* temperature curves measured at a low magnetic field by a vibrating sample magnetometer.

3. Results and discussion

The formation of the 2:17 phase is sensitive to the quenching rate. We obtained samples of $R_2Fe_{17}C_y$ ($y = 1.5$, 2.0 and 2.5) with quenching rates between 10 and 20 m s^{-1}. X-ray powder diffraction patterns show that these as-quenched samples are approximately single phase, crystallizing in the hexagonal Th_2Ni_{17}-type or rhombohedral Th_2Zn_{17}-type structure. The samples with higher carbon concentration contain some α-Fe as an impurity phase. Table 1 lists the volume V of $R_2Fe_{17}C_y$

0925-8388/93/$6.00

TABLE 1. Volume V (Å^3) of $R_2Fe_{17}C_y$ compounds

$R_2Fe_{17}C_y$	$y=1.5$	$y=2.0$	$y=2.5$
Y	536.7	541.3	
Gd	542.9	545.3	
Tb	537.4	543.3	546.3
Dy	536.4	543.1	546.7
Ho	533.9	539.1	543.3
Er	531.2	536.9	544.9

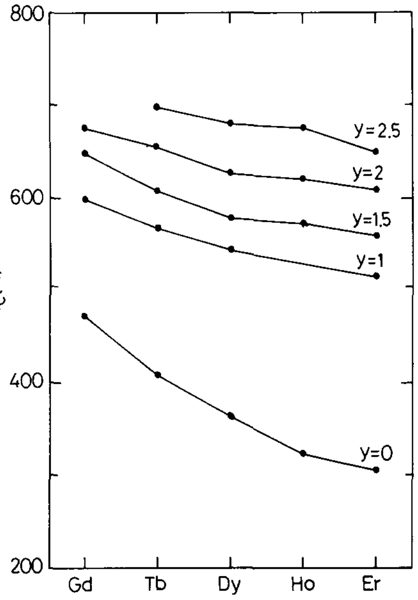

Fig. 1. Curie temperatures of $R_2Fe_{17}C_y$ with $y=0.0$, 1.0, 1.5, 2.0 and 2.5. The data of R_2Fe_{17} are taken from ref. 2.

compounds. For comparison, we take V as the unit cell volume for hexagonal structures and two-thirds of the unit cell volume for rhombohedral structures. The volumes show an increase with carbon content.

The Curie temperatures of $R_2Fe_{17}C_y$ at different carbon contents are shown in Fig. 1. By using the Curie temperature, we can estimate the strengths of the exchange interactions. According to the molecular field model, in the rare earth–iron compounds there are three main types of interaction: R–R, R–Fe and Fe–Fe. In most cases the application of the model reveals that the R–R interaction, especially at high temperature, is weak and can usually be neglected relative to the R–Fe and Fe–Fe interactions [13, 14]. Therefore the Curie temperature can be expressed as

$$3kT_C = a_{FeFe} + [a_{FeFe}^2 + 4a_{RFe}a_{FeR}]^{1/2}$$

where

$$a_{FeFe} = Z_{FeFe}J_{FeFe}S_{Fe}(S_{Fe}+1)$$

and

$$a_{RFe}a_{FeR} = Z_{RFe}Z_{FeR}S_{Fe}(S_{Fe}+1)(g_R-1)^2J_R(J_R+1)J_{RFe}$$

The quantities Z_{FeFe}, Z_{RFe} and Z_{FeR} represent coordination numbers in the crystal structure. For the 2:17 structure, we find $Z_{FeFe}=9$, $Z_{RFe}=19$ and $Z_{FeR}=2$. Using the Curie temperatures of $Tb_2Fe_{17}C_y$ and $Er_2Fe_{17}C_y$ with $S_{Fe}=1.05$, we calculated the exchange coupling constants J_{FeFe} and J_{RFe}. The results are summarized in Fig. 2. The value of J_{FeFe} increases significantly with the carbon content y, whereas J_{FeR} changes slightly with y. This suggests that the interstitial carbon atoms strongly enhance the Fe–Fe interaction and have little influence on the R–Fe interaction.

Generally the R–Fe moment coupling is considered to proceed via the 3d–5d and 5d–4f interaction [13]. In a first approximation, the 3d–5d interaction is expected to vary as $d_1=d_{RFe}-r_R-r_{Fe}$, whereas the 5d–4f interaction may vary as $d_2=r_R-r_{4f}$. Here d_{RFe} is the distance between R and Fe atoms, and r_{4f} is approximated by $\langle r_{4f}^2\rangle^{1/2}$. r_R and r_{Fe} are the metallic radii of the R and Fe atoms respectively. The introduction of C atoms in $R_2Fe_{17}C_y$ mainly leads to an increase in r_{RFe}. The dependence of J_{RFe} on the carbon content indicates that the R–Fe interaction is not sensitive to r_{RFe}. This is not surprising because the 5d electron wavefunctions have a larger spatial extent.

By comparison of the J_{FeFe} and J_{RFe} values in Fig. 2, it can be seen that the Fe–Fe interaction is the

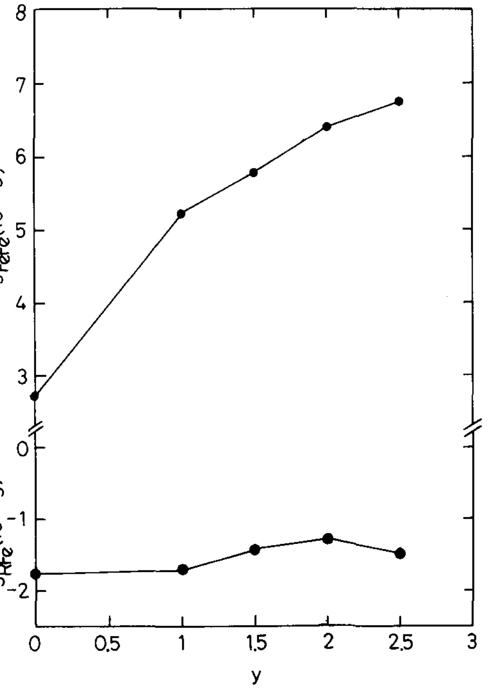

Fig. 2. Variation in J_{FeFe} and J_{RFe} as a function of the C content for $R_2Fe_{17}C_y$.

dominant contribution in determining the Curie temperature, as generally observed in most R–Fe intermetallics.

Figure 3 shows a plot of the volume dependence of the Curie temperature for the carbides $R_2Fe_{17}C_y$ with $y=1.0$–2.5. The relationship between T_C and volume is almost linear and independent of the rare earth. Figure 4 shows the variation in T_C as a function of volume for Y_2Fe_{17}, $Y_2Fe_{17}C_y$ and $Y_2Fe_{17}N_{2.7}$. Although the interstitial atoms are different, the carbides and the nitride show the same volume dependence of T_C. From Figs. 3 and 4 it can be seen that the Curie temperatures are not sensitive to the chemical composition.

The Curie temperatures of the R_2Fe_{17} compounds decrease strongly under applied pressure. If the value of $\Gamma = \mathrm{d}\ln T_C/\mathrm{d}\ln V$ is taken to be 14 for Y_2Fe_{17} [8], a good agreement between the pressure dependence of T_C and the volume dependence of T_C after the introduction of C or N is observed. All of these results show that the Curie temperature enhancement is primarily caused by the volume expansion.

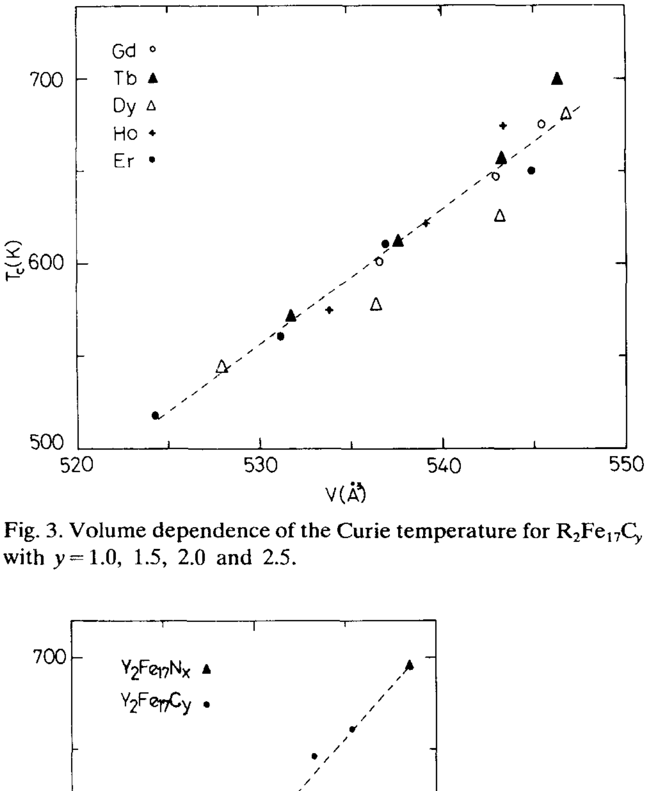

Fig. 3. Volume dependence of the Curie temperature for $R_2Fe_{17}C_y$ with $y=1.0$, 1.5, 2.0 and 2.5.

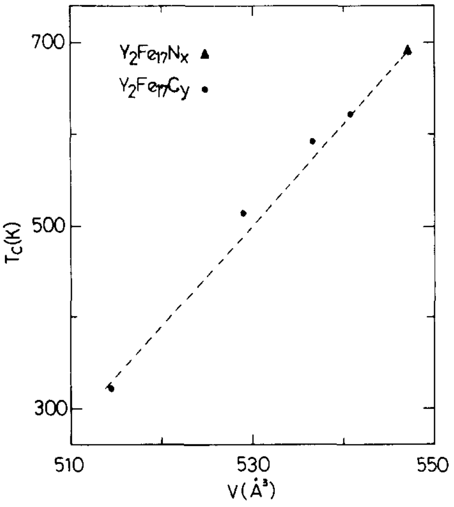

Fig. 4. Volume dependence of the Curie temperature for Y_2Fe_{17}, $Y_2Fe_{17}C_y$ and $Y_2Fe_{17}N_{2.7}$. The broken line represents the pressure dependence taken from ref. 8.

Since the Curie temperature of $R_2Fe_{17}C_y$ is mainly determined by the Fe–Fe interaction, the volume effect of T_C implies that the Fe–Fe interaction is sensitive to the interatomic spacing. This may reflect the localized character of Fe moments. Early investigations have shown localized Fe behaviour [14]. As opposed to the R–Co and R–Ni compounds, the binary R–Fe compounds show an increase in Curie temperature as the Fe concentration decreases. It seems that the exchange interaction is enhanced by dilating the Fe atoms with the R atoms. In addition, various exotic non-collinear spin structures occur in Lu_2Fe_{17}, Ce_2Fe_{17}, (Y, Th)Fe_3 and Th(Fe, Co)$_5$ for high Fe contents. This anomalous behaviour in R–Fe systems is considered to be connected with the more localized nature of the Fe moments.

Another special feature of R_2Fe_{17} compounds revealed by thermal expansion measurements [15] may also be taken as an indication of a volume effect on the Fe–Fe interaction. In contrast with Y_2Co_{17} and Y_2Ni_{17}, Y_2Fe_{17} has a negative thermal expansion coefficient below T_C. In order to minimize the total energy, the magnetic contributions from the exchange interactions are believed to decrease due to the volume expansion at low temperature.

From the experimental results mentioned above, it can be concluded that for rare earth–iron compounds with the 2:17 structure the Fe–Fe interaction is strongly dependent on the unit cell volume. The introduction of small atoms, such as H, C and N, into the 2:17 compounds produces volume expansion which increases the Fe–Fe interaction and the Curie temperature.

References

1 J. M. D. Coey and H. Sun, *J. Magn. Magn. Mater.*, *87* (1990) L251.
2 K. H. J. Buschow, R. Coehoorn, D. B. de Mooij, C. de Waard and T. H. Jacobs, *J. Magn. Magn. Mater.*, *92* (1990) L35.
3 K. Schnitzke, L. Schultz, J. Wecker and M. Katter, *Appl. Phys. Lett.*, *57* (1990) 2853.
4 J. M. D. Coey, H. Sun, Y. Otani and D. P. F. Hurley, *J. Magn. Magn. Mater.*, *98* (1991) 76.
5 M. Katter, J. Wecker, L. Schultz and R. Grossinger, *J. Magn. Magn. Mater.*, *92* (1990) L14.
6 H.-S. Li and J. M. Cadogan, *Solid State Commun.*, *80* (1991) 905.
7 R. Coehoorn, M. W. Dirken and K. H. J. Buschow, *Phys. Rev. B*, *42* (1990) 4645.
8 J. P. Liu, K. Bakker, F. R. De Boer, T. H. Jacobs, D. B. de Mooij and K. H. J. Buschow, *J. Less-Common Met.*, *170* (1991) 109.

9 J. M. D. Coey, H. Sun and D. P. F. Hurley, *J. Magn. Magn. Mater., 101* (1991) 310.

10 X. P. Zhong, R. J. Radwanski, F. R. de Boer, T. H. Jacobs and K. H. J. Buschow, *J. Magn. Magn. Mater., 86* (1990) 333.

11 B.-G. Shen, L.-S. Kong and L. Cao, *Solid State Commun., 83* (1992) 753.

12 L. Cao, L.-S. Kong and B.-G. Shen, *J. Phys. Condens. Matter, 4* (1992) L515.

13 K. H. J. Buschow, *Rep. Prog. Phys., 54* (1991) 1123.

14 H. R. Kirchmary and C. A. Poldy, *J. Magn. Magn. Mater., 8* (1978) 1.

15 D. Givord and R. Lemaire, *IEEE Trans. Magn., 10* (1974) 109.