Effect of Mo content on the structure stability of R3(Fe,Co,Mo)29
W. X. Li, L. Z. Cao, J. Shen, N. X. Chen, B. D. Liu et al.

Citation: J. Appl. Phys. 93, 6921 (2003); doi: 10.1063/1.1541637
View online: http://dx.doi.org/10.1063/1.1541637
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v93/i10
Published by the American Institute of Physics.

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors
Effect of Mo content on the structure stability of $R_3(\text{Fe,Co,Mo})_{29}$

W. X. Li
Institute of Physics, University of Science and Technology, Beijing 100083, China

L. Z. Cao, J. Shen, and N. X. Chen
Institute of Physics, University of Science and Technology, Beijing 100083, China

B. D. Liu, J. L. Wang, G. H. Wu, and F. M. Yang
State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Y. X. Li
School of Material Science and Engineering, Hebei University of Technology, Tianjin, 300130, China

(Received on 12 November 2002)

Formation of Ce$_3$Fe$_{29-x-y}$Co$_x$Mo$_y$ ($x=0, 3, 6, 10$) compounds has been investigated by means of x-ray diffraction and magnetic measurements. It is found that the required Mo content to stabilize the 3:29 compounds decreases monotonically as Co content increases, totally different from the discovery in the Gd$_3$(Fe$_{1-x}$Co$_x$)$_{29-y}$Cr$_y$ compounds. Meanwhile, we adopted a lattice inversion method in acquiring the interatomic potentials to rare-earth-transition metal intermetallic compounds, and investigated the substitution behaviors of Mo, Cr, V, and Mn in Fe-based and Co-based 3:29 compounds, respectively, by combining these potentials with computer simulation.

The calculated results show that the required Mo content in R$_3$Co$_{29-y}$Mo$_y$ compounds is lower than that in R$_3$Fe$_{29-y}$Mo$_y$ compounds, whereas the Cr content in R$_3$Co$_{29-y}$Cr$_y$ compounds higher than that in R$_3$Fe$_{29-y}$Cr$_y$ compounds, coinciding well with the previous discovery and the experimental results in this work. © 2003 American Institute of Physics. [DOI: 10.1063/1.1541637]

I. INTRODUCTION

Yang et al. and Wang et al. found that Gd$_3$(Fe$_{1-x}$Co$_x$)$_{29-y}$Cr$_y$ compounds possess easy-axis-type anisotropy at room temperature for $x \approx 0.4$. However, in these compounds, the amount of Cr needed for stabilization of the crystal structure is very large and increases with Co content, which leads to an unfavorable decrease of the Curie temperature and the saturation magnetization. On the other hand, it was found that in the R$_3$Fe$_{29-y}$Mo$_y$ compounds, the required Mo content is very small, which is important because in this case, the magnetic properties are only slightly affected by the nonmagnetic Mo. However, the R$_3$Fe$_{29-y}$Mo$_y$ compounds exhibit an easy-plane type of anisotropy and can therefore not be used as a starting material for the production of permanent magnets. In order to investigate the effect of Mo content on the structure stability of R$_3$(Fe,Co,Mo)$_{29}$ compounds, we synthesized the Ce$_3$Fe$_{29-y}$Co$_x$Mo$_y$ compounds ($x=0, 3, 6, 10$) and studied the substitution behaviors of Mo in these compounds. In this article, the effect of Mo content on the structure stability of R$_3$(Fe,Co,Mo)$_{29}$ compounds is presented in comparison with the substitution behavior of Cr in the Gd$_3$(Fe$_{1-x}$Co$_x$)$_{29-y}$Cr$_y$ compounds.

II. EXPERIMENT

Ce$_3$Fe$_{29-y}$Co$_x$Mo$_y$ ($x=0, 3, 6, 10$) compounds were prepared as similar reports before. After the arc melting process, as-cast ingots were sealed in evacuated quartz tubes and annealed for 72 h at 1373 K for $x=0$, at 1393 K for $x=3$, 1413 K for $x=6$, and at 1433 K for $x=10$. X-ray diffraction (XRD) with Cu Ka radiation was used to identify the phase and to determine the lattice parameters of the compounds. The thermomagnetic analysis (TMA) was performed by using a vibrating sample magnetometer in a low field of about 0.05 T in the temperature range from liquid-nitrogen temperature to above the Curie temperature.

III. RESULTS AND DISCUSSION

Based on XRD and TMA measurements, we investigated the phase formation range of Ce$_3$Fe$_{29-y}$Co$_x$Mo$_y$ ($x=0, 3, 6, 10$) compounds. As an example, Fig. 1 shows the thermomagnetic curves [Figs. 1(a)–1(c)] and the corresponding XRD patterns [Figs. 1(d)–1(f)] of Ce$_3$Fe$_{26.5}$Co$_{0.5}$Mo$_y$ ($y=0.7, 1.3, 1.7$). For $y=1.3$, the investigated sample is almost single phase and crystallizes in the Nd$_3$(Fe,Ti)$_{29}$-type of structure, as shown in Figs. 1(b) and 1(e). Second phases besides the main 3:29 phase were observed when the value of $y$ deviates much from 1.3. The second phase is 2:17 phase for $y=0.7$ as shown in Figs. 1(a) and 1(d), and 1:12 phase for $y=1.7$ as shown in Figs. 1(c) and 1(f).

In order to precisely investigate the formation range of the 3:29 phase, for a certain $x$, the samples with a wide range of $y$ values were prepared. Figure 2 shows the phase formation range of Ce$_3$Fe$_{29-y}$Co$_x$Mo$_y$ ($x=0, 3, 6, 10$). It can be seen that there appears to be a mixture of 1:12 + 3:29 phases when Mo is superfluous, and a mixture of

--

*Electronic mail: leewx@aphy.iphy.ac.cn*
2:17 + 3:29 phases when Mo is scarce. It is easily found that the range of 3:29 phase is narrow and becomes narrower as the Co content increases. Moreover, it is clearly shown in Fig. 2 that the required Mo content to stabilize the 3:29 compounds decreases monotonically as Co content increases. This result is totally different from our discovery in the Gd$_3$(Fe$_{1-x}$Co$_x$)$_{29-2y}$Cr$_y$ compounds, where the required Cr content increases as Co content increases.

To understand the changes of the required stabilizing element content with Co content in the $R_3$Fe$_{29-2x}Co_xM_y$ compounds, we theoretically investigated the behaviors of substitution Mo, Cr, V, and Mn in binary Fe-based and Co-based 3:29 compounds, by means of the simulation research based on *ab initio* effective pair potentials obtained through Chen’s lattice inversion method. 5–9 The metastable Nd$_3$T$_{29}$ (T=Co or Fe) structures used in the calculation were obtained by means of the same methods used in our former work.10 A periodical cell [([Nd$_3$T$_{29}$]$_2$)$_2$ x 2] containing 2 x 2 x 2 x 64 atoms were taken as a calculation unit. In the process of simulation, first, we substituted $M$ atoms for $T$ (Co or Fe) in some sites with different content, and then the energy minimization was applied to relax the ternary system under the interaction of effective potentials. The method used here for energy minimization is a conjugate gradient method with a cutoff radius of 14 Å.

Figure 3 shows crystal cohesive energy as a function of ternary element content $x$ in Nd$_3$Fe$_{29-2x}$M$_x$ and Nd$_3$Co$_{29-2x}$M$_x$ compounds with $M$ = Cr, Mo, V, and Mn. The results shown in Fig. 3 are the statistical average of 100 calculation samples. It can be seen that for $M$ = Cr, Mo, V, and Mn the cohesive energy decreases with the stabilizing element content, illustrating that each of these elements can stabilize the crystal structure and, correspondingly, the stabilized phases exist, in agreement well with the experimental results.1–4
As an example, Fig. 4 shows the comparison of crystal cohesive energy variation in \( \text{Nd}_3\text{Fe}_{29-x}\text{Mo}_x \) and \( \text{Nd}_3\text{Co}_{29-x}\text{Mo}_x \) (\( M = \text{Mo} \) and \( \text{Cr} \), \( x = 1 \)) with \( M \) occupying different \( T \) sites. Here, we suppose that all the \( M \) atoms occupy only the same site. It is found in Fig. 4 that for both Mo and Cr, the ternary element has the same site preference in Co-based as in the Fe-based compounds, and the preferential sites are \( \text{Fe}^7 (4i_2) \), \( \text{Fe}^6 (4i_1) \) and \( \text{Fe}^3 (4g) \). The difference among the three sites is very small, and even the difference between the three sites and the other eight \( T \) sites is little. Hence, it is obviously seen that, in addition to the three preferable sites, \( M \) may occupy some of the other eight \( T \) sites in these compounds. It is clearly shown in Fig. 4(a) that the total energy decline in all of the \( T \) sites, for Mo, is more evident in Fe-based 3:29 compounds than that in Co-based 3:29 compounds. In this case, compared with that in a Co-based 3:29 compound, the Mo substitution for \( T \) in an Fe-based 3:29 compound leads to much more energy decline and, then, the Fe-based 3:29 structure is more stable which allows one to introduce extra Mo occupying other relatively unfavorable \( T \) sites. This means that the solubility of Mo in \( \text{Nd}_3\text{Fe}_{29-x}\text{Mo}_x \) compounds should be higher than that in \( \text{Nd}_3\text{Co}_{29-x}\text{Mo}_x \). But for Cr, the total energy decline is more evident in Co-based 3:29 compounds than that in Fe-based 3:29 compounds as shown in Fig. 4(b), so Cr has a higher solubility in \( \text{Nd}_3\text{Co}_{29-x}\text{Cr}_x \) than in \( \text{Nd}_3\text{Fe}_{29-x}\text{Cr}_x \). The calculated results for Mn are similar to that for Cr, which agree well with experimental data that Mn has a much higher solubility (~72 at %) in \( \text{Pr}_3\text{Co}_6\text{Mn}_{23} \) compound, compared with the solubility of 33 at. % in \( \text{Nd}_3\text{Fe}_{18.3}\text{Mn}_{10.7} \) compounds. The calculated results also coincide qualitatively with our previous discovery in Cr-based compounds\(^2\) and the experimental results on Mo in this work. These results show that it is promising to search a material with high magnetic properties in the \( \text{R}_3\text{Fe}_{29-x}\text{Cr}_x\text{Mo}_y \) compounds, due to the low nonmagnetic Mo content in these compounds.

ACKNOWLEDGMENTS

The authors acknowledge the support of the State Key Project of Fundamental Research under Grant No. G2000067106.