

**ac-susceptibility studies on  $Zr_{1-x}Ho_xCo_2$  [ $0 \leq x \leq 1$ ] system and their hydrides**

R. Ramesh, M. S. Ramachandra Rao, and K. V. S. Rama Rao

Citation: *Journal of Applied Physics* **77**, 2090 (1995); doi: 10.1063/1.358851

View online: <http://dx.doi.org/10.1063/1.358851>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/77/5?ver=pdfcov>

Published by the **AIP Publishing**

---

**Articles you may be interested in**

[A low temperature anomaly observed in off-stoichiometric Ni–Mn–Ga system studied by higher harmonic ac-susceptibility measurements](#)

*Appl. Phys. Lett.* **97**, 122505 (2010); 10.1063/1.3486155

[Spatially resolved measurements of the ferromagnetic phase transition by ac-susceptibility investigations with x-ray photoelectron emission microscope](#)

*Appl. Phys. Lett.* **96**, 122501 (2010); 10.1063/1.3360205

[Simple uniaxial pressure device for ac-susceptibility measurements suitable for closed cycle refrigerator system](#)

*Rev. Sci. Instrum.* **78**, 063906 (2007); 10.1063/1.2745726

[Concentration and temperature dependence of electrical resistivity in  \$Zr\_{1-x}Ho\_xCo\_2\$  \( \$0 \leq x \leq 1\$ \) intermetallic compounds and their hydrides](#)

*J. Appl. Phys.* **76**, 3556 (1994); 10.1063/1.357414

[Magnetic ordering in  \$UCoNiSi\_2\$  and  \$UCoCuSi\_2\$  studied by ac-susceptibility and neutron diffraction measurements](#)

*J. Appl. Phys.* **75**, 7134 (1994); 10.1063/1.356702

---



**Not all AFMs are created equal**  
**Asylum Research Cypher™ AFMs**  
**There's no other AFM like Cypher**

[www.AsylumResearch.com/NoOtherAFMLikeIt](http://www.AsylumResearch.com/NoOtherAFMLikeIt)

**OXFORD**  
INSTRUMENTS  
*The Business of Science®*

# ac-susceptibility studies on $Zr_{1-x}Ho_xCo_2$ [ $0 \leq x \leq 1$ ] system and their hydrides

R. Ramesh,<sup>a)</sup> M. S. Ramachandra Rao,<sup>b)</sup> and K. V. S. Rama Rao<sup>c)</sup>

*Magnetism and Magnetic Materials Laboratory, Department of Physics, Indian Institute of Technology, Madras-600 036, India*

(Received 6 July 1994; accepted for publication 1 November 1994)

The ac-susceptibility studies were carried out on the intermetallic compounds  $Zr_{1-x}Ho_xCo_2$  [ $0 \leq x \leq 1$ ] in the temperature range 13–300 K. The magnetic transition is found to be of the first-order type for  $HoCo_2$  ( $x = 1.0$ ) and second-order type for  $x = 0.4–0.9$ . No magnetic ordering is observed for  $x = 0.2$  down to 13 K and  $x = 0.0$  is found to be Pauli paramagnetic. The magnetic ordering temperature ( $T_C$ ) increases from about 13 K for  $x = 0.4$  to 77 K for  $x = 1.0$ . In addition, spin reorientation transitions are observed for  $x = 0.9$  and 1.0. On hydrogenation,  $T_C$  is found to decrease considerably in all compounds. Hydrogen absorption in these compounds is found to weaken the exchange interactions which can be attributed to charge transfer effects. © 1995 American Institute of Physics.

## I. INTRODUCTION

RETM<sub>2</sub> (RE=rare earth and TM=Fe, Co, and Ni) intermetallic compounds with cubic Laves phase structure are known to exhibit a variety of magnetic behavior determined by the position of the Fermi level in the density of states curves.<sup>1</sup> Fe possesses a permanent moment in REFe<sub>2</sub>, whereas Ni is nonmagnetic in RENi<sub>2</sub> and the Co moment in RECo<sub>2</sub> depends strongly on the RE element. Magnetism in RECo<sub>2</sub> compounds arises out of itinerant electron magnetism of the 3d electrons of Co induced by the localized 4f moments of the RE atoms.<sup>2,3</sup> In RECo<sub>2</sub> compounds with heavy RE elements, a moment of about 1  $\mu_B$  is induced on Co by the 4f molecular field.<sup>2,4</sup>

The transition from ferrimagnetic to paramagnetic state is of the first-order type for the Dy, Ho, and Er compounds and of the second-order type for the Gd and Tb compounds.<sup>5,6</sup> The occurrence of the first-order transition in  $HoCo_2$  has been attributed to collective metamagnetic transition of the 3d electrons,<sup>7</sup> which depends on the 4f moment. If the local 4f moments are diluted by substituting nonmagnetic atoms like Y, the nature of magnetic transition is altered.<sup>8,9</sup> Investigation on the magnetic and transport properties of  $(Y_{1-x}Ho_x)Co_2$  compounds have indicated that the first-order transition changes to second order and then to disorder as  $x$  is decreased from 1.0.<sup>8,10,11</sup>

Further, the absorption of hydrogen by the intermetallic compounds affects the magnetic properties considerably.<sup>12</sup> Enhancement of susceptibility,<sup>13</sup> reduction in the Co moment and Curie temperature,<sup>8,14</sup> and various other phenomena have been observed in metal hydrides, clearly indicating that the electronic structure is altered considerably.

Hydrogen absorption in RECo<sub>2</sub> and REFe<sub>2</sub> compounds leads to charge transfer between hydrogen and the 3d band, as suggested by Mössbauer experiments.<sup>15–17</sup> The charge transfer might cause modifications in the electronic structure

of the host materials and hence the magnetic properties as well. The magnetic and Mössbauer studies carried out on some RECo<sub>2</sub>H<sub>y</sub> compound indicated that the absorption of hydrogen leads to the formation of magnetically ordered 3d atom clusters whose presence may remain almost undetected in standard magnetic measurements.<sup>18,19</sup>

Recently, we have studied<sup>20</sup> the electrical resistivity of the system  $Zr_{1-x}Ho_xCo_2$  [ $0 \leq x \leq 1$ ] and analyzed the anomalies in terms of spin fluctuation scattering. The hydrogen absorption leads to a metal–semiconductor-like transition due to the charge effects. In order to study their magnetic properties, ac-susceptibility measurements were carried out on the system  $Zr_{1-x}Ho_xCo_2$  [ $0 \leq x \leq 1$ ] and their hydrides and the results are presented in this article.

## II. EXPERIMENTAL TECHNIQUE

The intermetallic compounds  $Zr_{1-x}Ho_xCo_2$  [ $0 \leq x \leq 1$ ] were prepared by arc melting the constituent elements under argon atmosphere and subsequently annealing at 900 °C for 10 days. X-ray diffraction studies showed that the materials have formed in single phase with C15-type Laves phase structure. The ac-susceptibility studies were carried out in the temperature range 13–300 K using a Sumitoma ac susceptometer working on the principle of mutual induction. An oscillating field of 2 Oe was applied and at a frequency of 300 Hz. The real and the imaginary parts of the ac susceptibility were recorded using phase-sensitive detection technique.

## III. RESULTS AND DISCUSSION

### A. $Zr_{1-x}Ho_xCo_2$ -host materials

Figure 1 shows the temperature variation of the real part ( $\chi'$ ) of the ac susceptibility ( $\chi_{ac}$ ) recorded for the system  $Zr_{1-x}Ho_xCo_2$  [ $0 \leq x \leq 1$ ] at a frequency of 300 Hz. The Curie temperature ( $T_C$ ) and the spin reorientation temperature ( $T_{sr}$ ) are marked in each curve as shown in Fig. 1. The  $\chi'(T)$  curves show a sharp increase at Curie temperature ( $T_C$ ) for  $x = 1.0$  and peaks for other Ho concentrations ( $x \leq 0.9$ ).

<sup>a)</sup>Electronic mail: phy2@iitm.ernet.in

<sup>b)</sup>Present address: Tata Institute of Fundamental Research, Colaba, Bombay-400 005, India.

<sup>c)</sup>Author to whom all correspondence should be addressed.

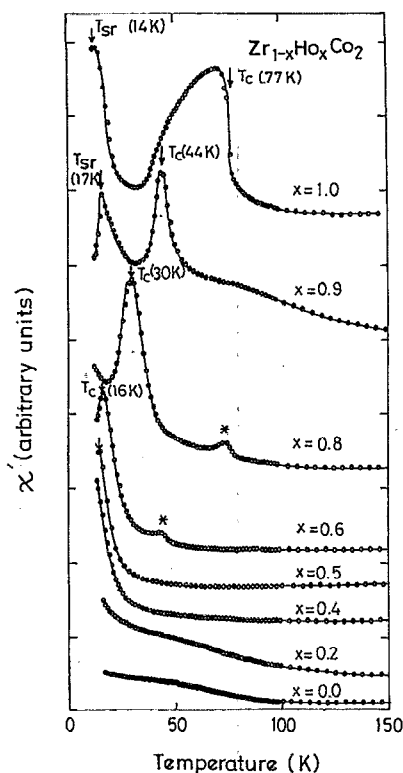


FIG. 1. Temperature variation of  $\chi''$  for the  $Zr_{1-x}Ho_xCo_2$  system. Curie temperature ( $T_C$ ) and spin reorientation temperature ( $T_{sr}$ ) are marked by arrows and the asterisk represents unidentified anomaly.

$HoCo_2$  undergoes a first-order transition at 77 K as suggested by several investigations on the temperature variation of lattice constant, transport, and magnetic properties.<sup>5-8</sup> On the other hand, peaks are observed for  $x=0.9, 0.8,$  and  $0.6$  over a temperature range, suggesting that the magnetic transitions are of the second-order type.

In the case of  $x=0.5$  and  $0.4$ , the onset of magnetic ordering is seen as an increase in  $\chi'$  at low temperatures.  $ZrCo_2$  ( $x=0.0$ ) shows a temperature-independent susceptibility characteristic of a Pauli paramagnet.<sup>21</sup> The  $\chi''(T)$  curves also show the various transitions at the same temperatures as observed in the  $\chi'(T)$  curves.

It can be seen from Fig. 1 that the  $T_C$  of the  $Zr_{1-x}Ho_xCo_2$  system increases with  $x$ . As Ho is gradually substituted in the Pauli paramagnetic  $ZrCo_2$ , the growing molecular field of Ho is expected to start inducing moment on Co and enhance the exchange interactions. The different types of magnetic ordering have also been observed in the electrical resistivity studies carried out on the  $Zr_{1-x}Ho_xCo_2$  system.<sup>20</sup>

As seen in Fig. 1, in addition to the peaks at the magnetic ordering temperatures, sharp peaks are observed at 14 and 17 K for the compounds  $HoCo_2$  and  $Zr_{0.1}Ho_{0.9}Co_2$ , respectively. These peaks correspond to the spin reorientation transitions occurring at the characteristic temperatures ( $T_{sr}$ ), which are marked by arrows in Fig. 1. During the process of cooling, a reorientation of the easy axis of magnetization from [100] to [110] has been reported for  $HoCo_2$  at 14 K

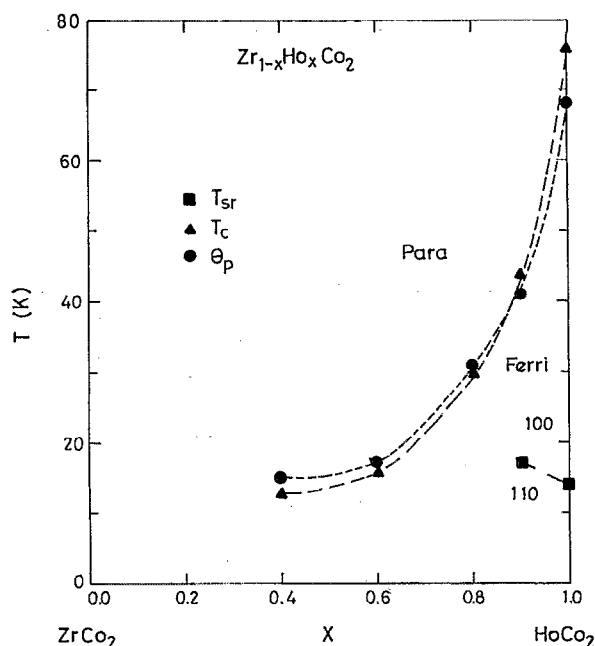


FIG. 2. Magnetic phase diagram for the  $Zr_{1-x}Ho_xCo_2$  system.

from magnetic and electrical resistivity<sup>8</sup> measurements. This has been explained by the combined effect of the crystalline field and exchange interactions.<sup>22</sup> The spin reorientation transition in the system  $Zr_{1-x}Ho_xCo_2$  increases with decrease of  $x$  and disappears for  $x \leq 0.8$  as seen in Fig. 1. Similar behavior has also been reported for the  $Y_{1-x}Ho_xCo_2$  system.<sup>22</sup>

Besides these transitions of magnetic origin, small maxima (anomalies) are observed in the  $\chi'(T)$  and  $\chi''(T)$  curves for  $x=0.6$  and  $0.8$  at 42 and 73 K, respectively, and are marked by an asterisk as shown in Fig. 1. With the available information, the origin of these anomalies in the paramagnetic temperature region is not known. A similar type of unidentified maxima in the paramagnetic region has also been reported in the ac-susceptibility studies on  $U_2NiSi_3$  system.<sup>23</sup>

The concentration dependence of the magnetic transition temperatures in the system  $Zr_{1-x}Ho_xCo_2$  is given in the form of a magnetic phase diagram as shown in Fig. 2. The Curie temperatures ( $T_C$ ) and the spin reorientation temperatures ( $T_{sr}$ ) are determined from the peak positions in the  $\chi'(T)$  curves and the paramagnetic Curie points ( $\theta_p$ ) are determined from the  $1/\chi$  vs  $T$  plots in the paramagnetic temperature regions. The values of the various transition temperatures are given in Table I. As can be seen from this table, both  $T_C$  and  $\theta_p$  increase with  $x$ . The  $T_C$  values are lower than  $\theta_p$  for  $x=0.4, 0.6,$  and  $0.8$ . For  $x=1.0$ , the higher value of  $T_C$  compared with  $\theta_p$  could be due to the first-order transition wherein  $\chi'$  increases sharply with decreasing temperature. The higher value of  $T_C$  for  $x=0.9$  could also be due to the sharp peak observed.

In the  $Zr_{1-x}Ho_xCo_2$  system,  $ZrCo_2$  is Pauli paramagnetic and magnetic ordering is observed for the concentration  $x \geq 0.4$ . As seen from Fig. 2,  $T_C$  increases sharply for

TABLE I. Variations in  $T_C$ ,  $\theta_p$ , and  $T_{sr}$  with  $x$  in the system  $Zr_{1-x}Ho_xCo_2$ .

$x$	$T_C(K)$	$\theta_p(K)$	$T_{sr}(K)$
0.0	...	...	...
0.2	...	...	...
0.4	~13	15	...
0.6	16	17	...
0.8	30	31	...
0.9	44	41	17
1.0	77	68	14

$x \geq 0.8$ , indicating the onset of strong exchange interactions caused by the  $4f$  molecular field of the substituted Ho atoms. In  $HoCo_2$ , the  $4f$  moments are known to induce a metamagnetic transition on the Co atoms.<sup>7</sup>  $HoCo_2$  is ferrimagnetic with Co moment of about  $1 \mu_B$  induced by the molecular field of Ho.<sup>2</sup>

The ac-susceptibility measurements were carried out at three different frequencies viz. 10, 300, and 900 Hz and at a constant field strength of 2 Oe. It is found that the positions of the anomalies observed for  $x=0.6$  and  $0.8$  are independent of frequency of the applied oscillating field excluding the possibility of considering them as to be due to spin glass behavior.

### B. $Zr_{1-x}Ho_xCo_2H_y$ hydrides

The ac-susceptibility studies carried out on the hydrides of  $Zr_{1-x}Ho_xCo_2$  indicate the suppression of magnetic interactions. The temperature variation of  $\chi'$  for the  $Zr_{0.6}Ho_{0.4}Co_2H_y$  compounds shows that the magnetic transi-

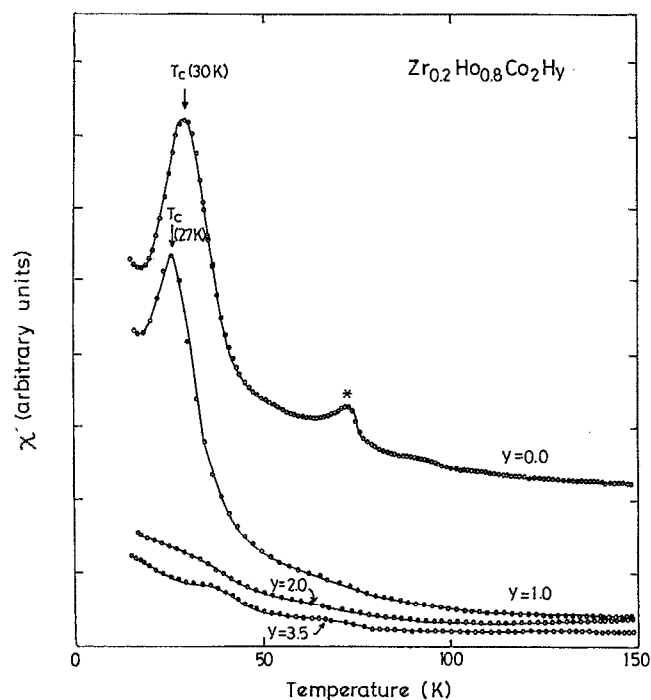


FIG. 3. Temperature variation of  $\chi'$  for  $Zr_{1-x}Ho_xCo_2H_y$ . Arrows represent  $T_C$  and the asterisk represents unidentified anomaly.

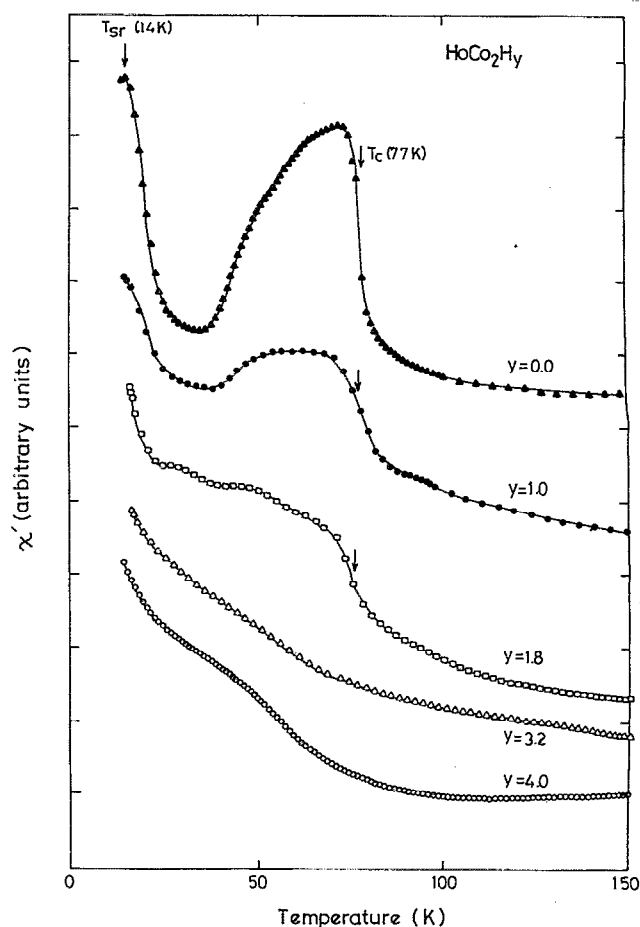


FIG. 4. Temperature variation of  $\chi'$  for  $HoCo_2H_y$ . Curie temperature ( $T_C$ ) and spin reorientation temperature ( $T_{sr}$ ) are marked by arrows.

tion is not altered up to a hydrogen concentration of  $y=2.3$ . However, for  $Zr_{0.4}Ho_{0.6}Co_2H_y$ , the peak observed at  $T_C$  disappears for  $y=2.3$ . Figure 3 shows the temperature variation of  $\chi'$  for the compound  $Zr_{0.2}Ho_{0.8}Co_2H_y$ . The magnetic transition temperature, marked by an arrow in Fig. 3, is not altered much for the concentration  $y=1.0$  and disappears for  $y \geq 2.0$ . Similar behavior is observed for  $HoCo_2H_y$  as shown in Fig. 4. The first-order magnetic transition observed for  $HoCo_2$  at 77 K is retained in  $HoCo_2H_y$  up to a concentration of  $y=1.8$  and for  $y > 1.8$  there is no indication of a magnetic transition at temperatures down to 13 K. Similar behavior is observed in the  $\chi''(T)$  curves. This effect has also been observed in the electrical resistivity measurements on the  $Zr_{1-x}Ho_xCo_2H_y$  system.<sup>20</sup>

Reduction in  $T_C$  and the suppression of magnetic interactions seems to be the consequence of modifications in the electronic band structure of the host materials.<sup>24</sup> In  $RECo_2$  compounds, the  $3d$  band is partially unfilled and the Fermi level lies in the sharply decreasing portion of the density of states curves,<sup>1</sup> resulting in an induced moment on Co by the molecular field of RE. In  $RECo_2$  compounds, the  $3d$  band is probably filled by the electrons donated by the absorbed hydrogen.<sup>17,25,26</sup> It is probable that the  $T_C$  does not get altered as long as the  $3d$  band is unfilled. In the case of

Zr<sub>1-x</sub>Ho<sub>x</sub>Co<sub>2</sub>H<sub>y</sub> compounds with higher Ho concentrations, the 3d band probably remains unfilled up to y=2.0 and therefore T<sub>C</sub> remains unaltered up to y=2.0 as seen from the Figs. 3 and 4.

When the 3d band is completely filled, Co becomes non-magnetic and Ho can no longer induce moment on Co. Thus, Ho will be the only moment carrying species which can determine the magnetic ordering temperatures. Further increase in the hydrogen concentration in these compounds might weaken the RE-RE exchange interactions<sup>27</sup> thereby causing a large decrease in T<sub>C</sub>. Such phenomena are observed for y ≥ 2.0 where no magnetic transition is observed down to 13 K. The modifications in the electronic structure brought about by the charge transfer effects are also observed from the electrical resistivity studies on Zr<sub>1-x</sub>Ho<sub>x</sub>Co<sub>2</sub>H<sub>y</sub> compounds, which revealed a metal-semiconductor-like transition on hydrogen absorption.<sup>20</sup>

## ACKNOWLEDGMENTS

This work was supported by the Ministry of Non-Conventional Energy Sources, Government of India. The authors thank Dr. U. V. Varadaraju for discussions. One of the authors (R. R.) is grateful to Indian Institute of Technology, Madras, for financial assistance.

<sup>1</sup>M. Cyrot and M. Lavagna, *J. Phys.* **40**, 763 (1979).

<sup>2</sup>R. M. Moon and W. C. Koehler, *J. Appl. Phys.* **36**, 978 (1965).

<sup>3</sup>E. Burzo, *Phys. Rev.* **6**, 2882 (1972).

<sup>4</sup>K. N. R. Taylor, D. Melville, and G. J. Primavesi, *J. Phys. F: Metal Phys.* **2**, 584 (1972).

<sup>5</sup>D. Block, D. M. Edwards, M. Shimizu, and J. Voiron, *J. Phys. F: Metal Phys.* **5**, 1217 (1975).

<sup>6</sup>J. Inoue and M. Shimizu, *J. Phys. F: Metal Phys.* **12**, 1811 (1982).

<sup>7</sup>R. Lemaire, *Cobalt* **33**, 201 (1966).

<sup>8</sup>W. Steiner, E. Gratz, H. Ortbauer, and H. W. Camens, *J. Phys. F: Metal Phys.* **8**, 1525 (1978).

<sup>9</sup>N. H. Duc, T. D. Hien, P. P. Mai, N. H. K. Ngan, N. H. Sinh, P. E. Brommer, and J. J. M. Franse, *Physica B* **160**, 199 (1989).

<sup>10</sup>E. Gratz, E. Bauer, V. Sechovski, and J. Chmista, *J. Magn. Magn. Mater.* **54-57**, 517 (1986).

<sup>11</sup>G. Hilscher, N. Pillmayr, C. Schmitzer, and E. Gratz, *Phys. Rev. B* **37**, 3480 (1988).

<sup>12</sup>W. E. Wallace, F. Pourarian, A. T. Pedziwiatr, and E. B. Boltich, *J. Less-Common Metals* **130**, 33 (1987).

<sup>13</sup>S. Hirosova, F. Pourarian, V. K. Sinha, and W. E. Wallace, *J. Magn. Magn. Mater.* **38**, 159 (1983).

<sup>14</sup>K. H. J. Buschow, P. C. P. Bouten, and A. R. Miedema, *Rep. Prog. Phys.* **45**, 937 (1982).

<sup>15</sup>R. L. Cohen, K. W. West, F. Oliver, and K. H. J. Buschow, *Phys. Rev. B* **21**, 941 (1980).

<sup>16</sup>S. Annapoorni and K. V. S. Rama Rao, *J. Appl. Phys.* **67**, 424 (1990).

<sup>17</sup>K. H. J. Buschow and A. M. van Diepen, *Solid State Commun.* **19**, 79 (1976).

<sup>18</sup>L. I. de Jongh, J. Bartolome, J. J. A. M. Greidanus, H. J. M. de Groot, H. L. Stipdonk, and K. H. J. Buschow, *J. Magn. Magn. Mater.* **25**, 207 (1981).

<sup>19</sup>K. H. J. Buschow and A. M. van der Kraan, *J. Less-Common Metals* **91**, 203 (1983).

<sup>20</sup>R. Ramesh and K. V. S. Rama Rao, *J. Appl. Phys.* **76**, 3556 (1994).

<sup>21</sup>H. Fujii, F. Pourarian, and W. E. Wallace, *J. Magn. Magn. Mater.* **24**, 93 (1981).

<sup>22</sup>E. Gratz and H. Nowotny, *J. Magn. Magn. Mater.* **29**, 127 (1982).

<sup>23</sup>D. Kaczorowski and H. Noel, *J. Phys. Cond. Mater.* **5**, 9185 (1993).

<sup>24</sup>M. Gupta and L. Schlapbach, in *Hydrogen in Intermetallic Compounds—I*, Topics in Applied Physics Vol. 63, edited by L. Schlapbach (Springer, Berlin, 1988), p. 139.

<sup>25</sup>K. H. J. Buschow and R. C. Scherwood, *J. Appl. Phys.* **49**, 1480 (1978).

<sup>26</sup>F. Pourarian, W. E. Wallace, and S. K. Malik, *J. Magn. Magn. Mater.* **25**, 299 (1982).

<sup>27</sup>M. Yamaguchi, in *Materials Science and Technology*, edited by K. H. J. Buschow (VCH, Weinheim, 1994), Vol. 3B.