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2001 J. Phys.: Condens. Matter 13 L747

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INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) L747–L752 PII: S0953-8984(01)24638-4

LETTER TO THE EDITOR

Magnetic entropy change in RCoAl (R = Gd, Tb, Dy, and Ho) compounds: candidate materials for providing magnetic refrigeration in the temperature range 10 K to 100 K

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Received 8 May 2001
Published 19 July 2001
Online at stacks.iop.org/JPhysCM/13/L747

Abstract

Large magnetic entropy changes were observed in RCoAl compounds, where R = Gd, Tb, Dy, and Ho, at their Curie temperatures. These RCoAl alloys have a hexagonal, $MgZn_2$ structure and their Curie temperatures fall in the temperature range 10–100 K. A 'table-like' behaviour was found in the temperature dependence of the magnetic entropy change ($-\Delta S(T)$) obtained in the soft magnetic GdCoAl alloys, which can be used either to fill up the gap (near 100 K) in the profile of magnetic entropy change versus temperature required by an eight-stage magnetic refrigerator or to complete an Ericsson circle. It has also been shown that soft ferromagnetic materials with Curie temperatures in the temperature range from 10 K to 100 K can be obtained by using multi-R elements instead of a single-R element in the RCoAl compounds.

Rare-earth elements and their alloys have been intensively studied recently in view of their large magnetocaloric effect (MCE), and have proved to be attractive candidate materials for providing magnetic refrigeration [1–3]. Since the size of the MCE is only significant in the vicinity of the transition temperatures of an ordered magnetic material, a number of magnetic materials have to be used to produce a magnetic refrigerator working over an extended temperature range—for example, from 20 K to 300 K. This is the so-called active magnetic regenerator refrigerator (AMRR), proposed and implemented by Barclay and Steyert in 1982 [4]. They suggested that a magnetic refrigerant acts simultaneously as a regenerator. Based on this concept, an eight-stage magnetic refrigerator was suggested by Gschneidner Jr and Pecharsky for the temperature range 10 K–300 K, although three necessary materials were lacking at that time [1]. Very recently we have found that TbGdAl [5] and LaFeM alloys (M = Si, Al,

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Co, etc) [6] are very good candidates for taking the roles of the three missing materials. The remaining materials chosen for the eight-stage refrigerator were the best among the materials existing at that time, but may no longer be the best choices. For example, GdSiGe alloys are better than those materials [7]. It remains a challenge to seek materials with larger MCEs at suitable temperatures.

It is well known that there are a great number of rare-earth intermetallic compounds with the composition 1:2. For example the series RM_2, whose crystallographic structures depend on the elements R (=rare-earth elements) and M (=other metal elements) [8]. Laves cubic compounds RAl_2 (R = heavy rare-earth elements, such as Gd, Tb, Dy, Ho, Er or their solid solutions) have been widely investigated [9–14, 5] in view of their large MCEs in the temperature range 15–170 K. It has been suggested that RAl_2 materials can substitute for the very expensive GdPd alloys used in AMRRs specifically for liquefying hydrogen gas [15, 16]. The MCEs in RNi_2 [13] and RNiAl [17,18] alloys have also been extensively investigated. In this letter, we report the promising magnetic entropy changes in the family of intermetallic compounds RCoAl (R = Gd, Tb, Dy, Ho) in the temperature range 10–100 K.

Samples of RCoAl (R = Gd, Tb, Dy, and Ho) were prepared by arc melting the raw materials with a purity of 99.9% under an argon atmosphere. To obtain high-quality and homogeneous materials, the ingots were arc melted several times. X-ray powder diffraction patterns show that RCoAl alloys crystallize in the hexagonal $MgZn_2$-type structure and no impurity phase was observed. The temperature and field dependences of the magnetizations were obtained by using a commercial SQUID magnetometer (Quantum Design MPMS-5S).

The Curie temperatures listed in table 1 were determined from the temperature-dependent magnetization measured in zero-field-cooled (ZFC) and field-cooled (FC) procedures [19] under a 100 Oe magnetic field; see figure 1. The values of T_C obtained are roughly consistent with those from previous studies [16]. Whereas the ZFC and FC curves obtained for GdCoAl

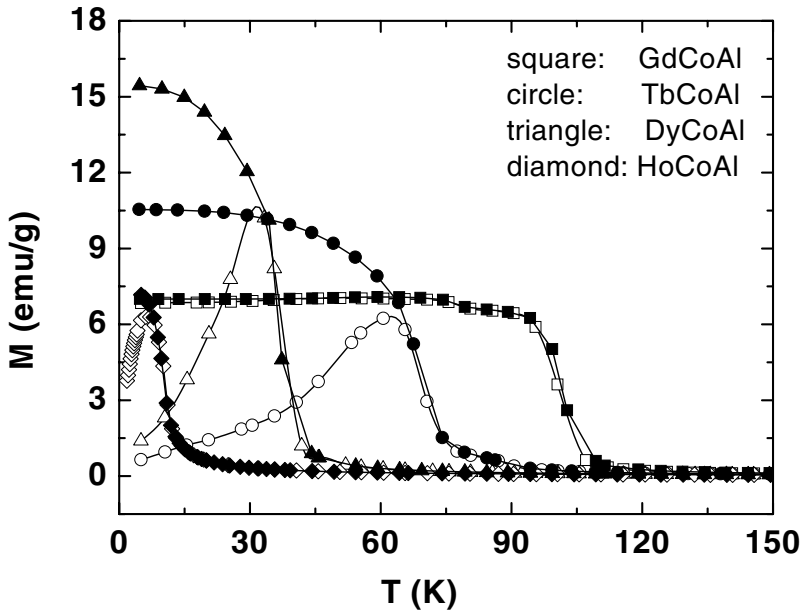

Figure 1. Magnetization as a function of temperature measured in the ZFC (open symbols) and FC (solid symbols) processes for the four alloys.

Table 1. Values of the Curie temperatures and the maximum magnetic entropy changes for all of the materials.

		$-\Delta S_M$ (J kg^{-1} K^{-1}) (maximum)	
Alloys	T_C (K)	$\Delta H = 2$ T	$\Delta H = 5$ T
GdCoAl	100	4.9	10.4
TbCoAl	70	5.3	10.5
DyCoAl	37	9.2	16.3
HoCoAl	10	12.5	21.5
$(Gd_{0.5}Dy_{0.25}Er_{0.25})CoAl$	45	6.3	14.0

alloy collapse onto a single curve over the whole temperature range, a significant thermal irreversibility between the ZFC and FC curves is observed at low temperatures for the alloys with R = Tb, Dy, and Ho. This irreversibility can be ascribed to the magnetic anisotropy in the TbCoAl, DyCoAl, and HoCoAl alloys. The relatively strong anisotropy in these three alloys is due to the large orbital angular momentum in Tb, Dy, and Ho atoms (or ions).

From general thermodynamic equations [2, 20], the magnetic entropy change for the isobaric–isothermal system can be calculated from the isothermal magnetization via

$$-\Delta S_M(T, H) = \int_0^H (\partial M/\partial T)_H \, \mathrm{d}H. \tag{1}$$

Using the magnetization data obtained at discrete values of field and temperature, the magnetic entropy change can be calculated approximately using the numerical formula [21]

$$-\Delta S_M = \sum_i \frac{1}{T_{i+1} - T_i}(M_i - M_{i+1})\,\Delta H_i \tag{2}$$

where M_i and M_{i+1} are the magnetization values at temperatures T_i and T_{i+1}, respectively, in a field H.

The isothermal magnetizations $M(H)$ were measured from 0 to 5 T with a field step of 0.1 T over a broad temperature range. The temperature interval between the isotherms is 5 K. The sweep rate of the field is slow enough for the $M(H)$ curves to be isothermal [5, 6, 20]. By using equation (2), the magnetic entropy change $-\Delta S_M(T, H)$ was obtained. Figures 2(b) and 2(a) plot $-\Delta S_M$ as a function of the temperature for the field changing from $H = 0$ to $H = 2$ and 5 T respectively (i.e. $\Delta H = 2$ and 5 T). It is observed that the maximum entropy changes are 10.4, 12.5, 16.3, and 21.5 J kg^{-1} K^{-1} with $\Delta H = 5$ T for the RCoAl alloys with R = Gd, Tb, Dy, and Ho, respectively. Even with $\Delta H = 2$ T, which can be provided by using a NdFeB permanent magnet, the maximum values of $-\Delta S_M$ are 4.9, 5.3, 9.2, 12.1 J kg^{-1} K^{-1}, respectively. These large entropy changes indicate that the RCoAl intermetallic compounds appear to be very attractive candidate materials for use in a magnetic refrigerator working in the temperature range 10–100 K.

It is noteworthy that a large, flat entropy change appears over the temperature range 70–105 K in the $-\Delta S_M(T)$ curve obtained for GdCoAl, whereas the $-\Delta S_M(T)$ curves obtained for the other three alloys show a normal 'caret-like' shape. This flat magnetic entropy change may give rise to a 'table-like' adiabatic temperature change similar to that observed in $(Gd_{0.54}Er_{0.46})NiAl$ [18], which satisfies the requirements of a magnetic refrigerator operating on an Ericsson cycle over this temperature range. This is at least as good as, or better than, the use of a series of materials to provide the same profile of magnetic entropy change versus temperature [18]. The GdCoAl compound is, therefore, a very attractive candidate refrigerant

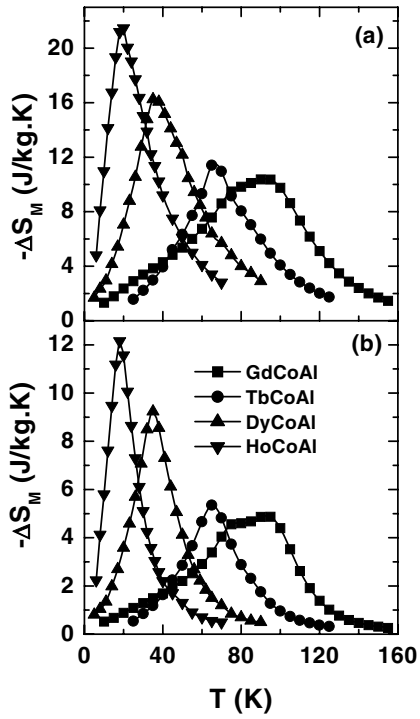

Figure 2. Magnetic entropy change as a function of temperature for different RCoAl alloys; (a) $\Delta H = 5$ T and (b) $\Delta H = 2$ T.

to fill the gap near 100 K in the ΔS versus temperature profile, as required by the eight-stage magnetic refrigerator suggested by Gschneidner Jr and Pecharsky [1].

The major application of a refrigerator working in the temperature range 10–80 K is to liquefy hydrogen gas. For a magnetic refrigerator working over this temperature range, one can use magnetic refrigerants, such as GdPd and $(Dy_{0.5}Er_{0.5})Al_2$ alloys that exhibit a maximum MCE at about 40 K. From our results in figure 2, it is clear that DyCoAl is a potential candidate. Owing to the strong anisotropy of dysprosium, however, a significant hysteretic behaviour has been observed at 5 K with a large coercive field (1 kOe) and a large ratio of remanent magnetization to saturation magnetization ($\sim$38%). The hysteretic behaviour will considerably lower the MCE in applications such as that as a magnetic refrigerant. In order to decrease the anisotropy and keep the Curie temperature unchanged, we fabricated a compound with the composition $(Gd_{0.5}Dy_{0.25}Er_{0.25})$CoAl. The element Er was used to cancel the anisotropy of Dy, since the Stevens factors of Dy and Er have opposite signs [22]. To maintain the Curie temperature, Gd is added to compensate for the reduction in Curie temperature due to the element Er.

The temperature dependence of the coercive field and the magnetization of the compound $(Gd_{0.5}Dy_{0.25}Er_{0.25})$CoAl are plotted in figure 3 and its inset. It is evident that the material is magnetically soft. The Curie temperature $T_C = 45$ K is slightly higher than that of DyCoAl. At 5 K, the coercive field is 150 Oe and thus much smaller than that, 1 kOe, for DyCoAl. The temperature dependence of the coercive field can be described by $H_c(T) = 268\exp(-5.2T/T_C)$ (Oe). Consequently the $(Gd_{0.5}Dy_{0.25}Er_{0.25})$CoAl alloy is a good ferromagnet and magnetically soft enough for application as a refrigerant.

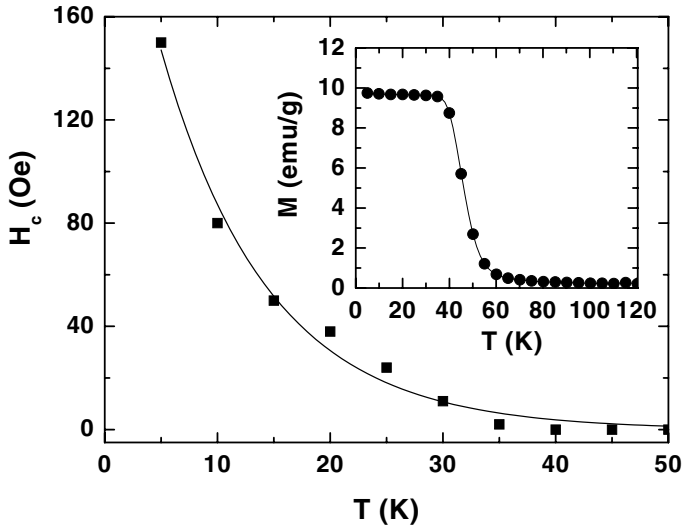

Figure 3. Coercive field as a function of temperature obtained in the $(Gd_{0.5}Dy_{0.25}Er_{0.25})CoAl$ alloy. The inset shows the temperature-dependent magnetization measured in a 100 Oe magnetic field.

Figure 4 shows the magnetic entropy change $-\Delta S_M$ of $(Gd_{0.5}Dy_{0.25}Er_{0.25})CoAl$ as a function of temperature. A relatively broad peak is found around the Curie temperature. The maximum $-\Delta S_M$ at the Curie temperature $T_C = 45$ K reaches 14.0 J kg^{-1} K^{-1} for a 5 T field change, comparable with that in $(Gd_{0.54}Er_{0.46})NiAl$ [18].

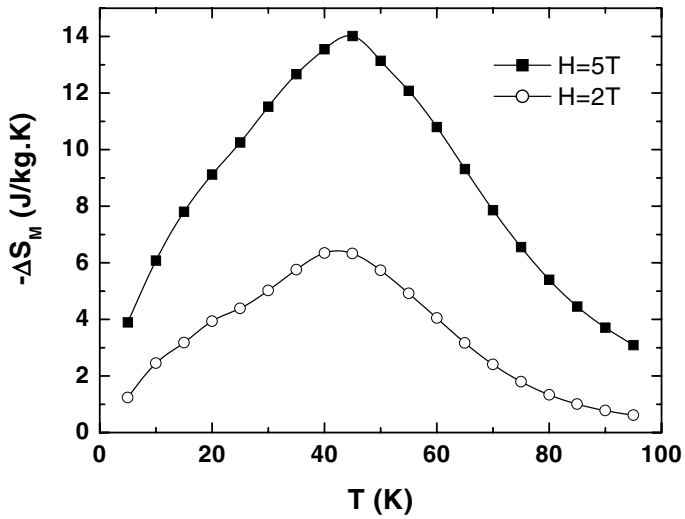

Figure 4. Temperature-dependent magnetic entropy change obtained in $(Gd_{0.5}Dy_{0.25}Er_{0.25})CoAl$ alloys for field changing from 0 to 2 and 5 T.

In summary, we have shown that the compounds RCoAl with hexagonal $MgZn_2$ structure show large magnetic entropy changes around their Curie temperatures in the temperature range 10–100 K, and in particular the GdCoAl alloy exhibits a 'table-like' magnetic entropy change,

which can be used either to fill up the gap (near 100 K) in the profile of magnetic entropy change versus temperature required by an eight-stage magnetic refrigerator or to complete an Ericsson circle. It has also been demonstrated that by using $(Gd)_X(Er)_Y(Dy)_Z$, $X+Y+Z=1$, to substitute for the single element R in RCoAl, soft magnetic materials with Curie temperatures in the range 10 K–100 K can be obtained.

This work was supported partially by Hong Kong RGC (HKUST6157/00E) and partially by the State Key Project of Fundamental Research of China.

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