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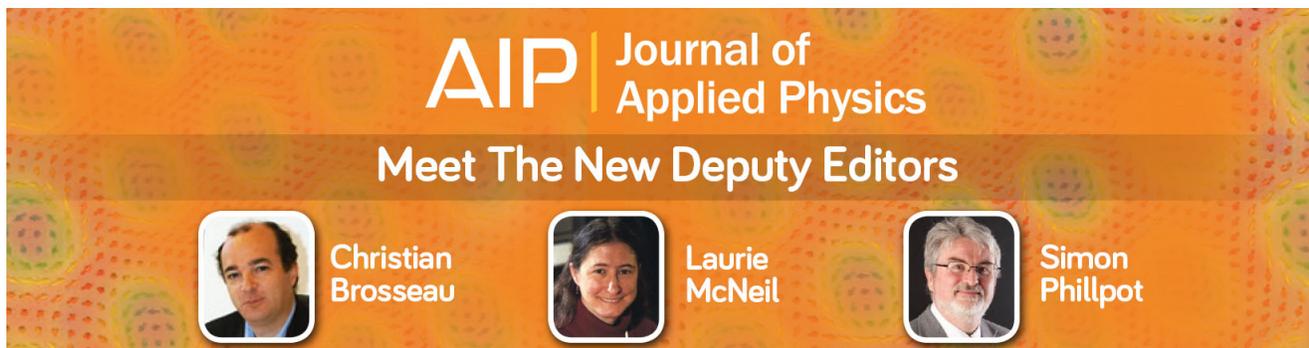
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Large reversible magnetocaloric effect in Er₃Co compound

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Magnetic and magnetocaloric properties of the intermetallic compound Er₃Co have been studied. Temperature dependence of magnetization data shows that it exhibits ferromagneticlike bulk magnetic ordering at 14 K. For field changes (ΔH) of 20 and 50 kOe, the maximum values of isothermal magnetic entropy change are found to be 9 and 17 J/kg K, respectively. For $\Delta H=20$ and 50 kOe, the relative cooling powers are found to be 140 and 450 J/kg, respectively. At temperatures above T_{ord} , the spin fluctuations are found to affect the magnetocaloric properties of Er₃Co. © 2010 American Institute of Physics. [doi:10.1063/1.3367887]

I. INTRODUCTION

Magnetic refrigeration is becoming a promising and viable technology for cryogenic applications.^{1–7} Apart from the ecofriendly nature, the efficiency of these refrigerators is estimated to be better than that of the conventional refrigerators. It is based on magnetocaloric effect (MCE), which is defined as the thermal response of a magnetic material to an applied field. MCE manifests itself as isothermal entropy change (ΔS_M) or as adiabatic temperature change (ΔT_{ad}) when the material is subjected to a changing magnetic field. In recent years, compounds showing giant MCE have been given the utmost attention in the search for potential magnetic refrigerants. After the discovery of giant MCE in Gd₅Si₂Ge₂,^{8,9} RCo₂-based compounds¹⁰ LaFe_{11.4}Si_{1.6},^{11,12} and MnAs,^{13,14} the attention has largely shifted to the magnetic materials showing field-induced magnetic transitions and/or structural transitions.

In our attempt to identify promising refrigerant materials suitable for various temperature regimes, we have studied the magnetic and magnetocaloric properties of the intermetallic compound Er₃Co. In general, the R₃Co compounds crystallize in the Fe₃C-type orthorhombic structure (space group Pnma) which is described by trigonal prisms with the corners occupied by R atoms and the center by a Co atom.^{6,15–19} The previous studies have shown that owing to the filling of the 3d band of Co by 6s and 5d electrons of R atoms, the Co sublattice is nearly nonmagnetic; however, the partial polarization of 3d band by the rare earth exchange field can lead to small moment at the Co site.^{15,20} Thus, the magnetic ordering of R₃Co compounds results from indirect interactions between R atoms through the conduction electrons. The low symmetry crystal field strongly influences the arrangement of magnetic moments.¹⁵

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II. EXPERIMENTAL DETAILS

The Er₃Co alloy was prepared by arc melting of the stoichiometric ratios of the constituent elements under argon atmosphere. The starting materials used were of more than 99.9% (wt %) purity. To ensure the homogeneity, the ingots were flipped upside down and melted several times and were annealed in a sealed quartz tube at 773 K for 1 week. The structural analysis of samples was carried out by the Rietveld (FULLPROF) refinement of the room temperature x-ray powder diffraction data collected using the Cu K α radiation. The annealed ingot Er₃Co was found to crystallize in the Fe₃C-type orthorhombic structure with lattice parameters $a = 6.912(1)$ Å, $b = 9.196(2)$ Å, and $c = 6.192(1)$ Å. Magnetization (M) measurements in the temperature (T) range of 2–200 K were carried out on a 14.6 mg irregularly shaped piece of alloys both under “zero field cooled” (ZFC) and “field cooled” (FC) conditions by using a vibrating sample magnetometer (Oxford instruments). Field (H) dependence of magnetization data was collected after reaching the desired temperature under ZFC condition. MCE was calculated using the M - H isotherms near the magnetic transition temperature.

III. RESULT AND DISCUSSION

Figure 1 shows the temperature (T) dependence of magnetization (M) data measured in an applied field of 200 Oe under ZFC and FC conditions. It may be noted that the magnetic correlations develop on cooling the sample and at about 14 K a ferromagneticlike transition takes place, which is in good agreement with the previous reports.^{16,17} The $M(T)$ data collected under ZFC and FC protocols show irreversibility. It is well known that the thermomagnetic irreversibility between the ZFC and FC $M(T)$ data is a typical feature associated with spin glass system; however, it may also be observed in ferromagnetic materials having large anisotropy, in materials with coexisting ferromagnetic and antiferromag-

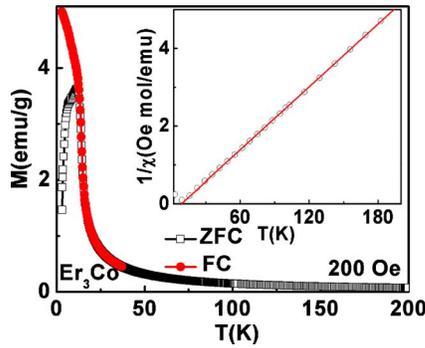


FIG. 1. (Color online) T dependence of M data of Er_3Co collected in a field of 200 Oe under ZFC and FC conditions. The inset shows the temperature variation of the inverse of susceptibility and the Curie–Weiss fit to it.

netic interactions.^{4,21} It is quite likely that the domain wall pinning is the reason for the thermomagnetic irreversibility in the present case.

Above 40 K, the susceptibility (χ) of Er_3Co obeys the Curie–Weiss law (see inset of Fig. 1) with the paramagnetic Curie temperature (θ_p) and effective moment (μ_{eff}) of 9 K and $9.9\mu_B/\text{Er}^{3+}$, respectively. The positive sign θ_p indicates that this compound possesses ferromagnetic interactions. The μ_{eff} is slightly more than the free ion value of $9.6\mu_B/\text{Er}^{3+}$. Such an excess μ_{eff} has been observed in a few other intermetallic compounds in which the polarization of the conduction electrons by the rare earth molecular field is considerable.^{15,20,22}

Figure 2 shows the field dependence of magnetization data collected during both increasing (black line) and decreasing (red line) fields at 2 K. We note that the $M(H)$ data show a rapid increase at low fields. However, at higher fields ($H > 40$ kOe), it varies linearly with field and does not saturate even at $H = 90$ kOe. Saturation magnetization (M_{sat}) calculated using the M versus $1/H$ plot is found to be $7\mu_B/\text{Er}^{3+}$, which is considerably lower than the gJ values of 9 expected for Er^{3+} ions. The low saturation value seen in Er_3Co may be attributed to the crystalline electric field effect.¹⁷ It may be noted that the $M(H)$ isotherms do not exhibit large hysteresis, implying that this compound is a soft ferromagnet.

MCE in Er_3Co has been determined in terms of isothermal magnetic entropy change (ΔS_M) by employing the integrated Maxwell's relation^{1,3}

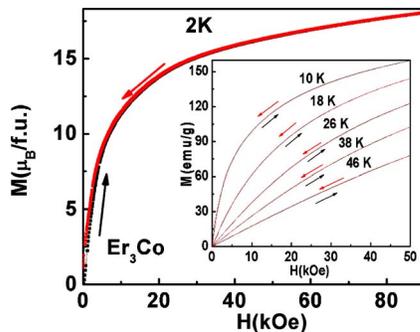


FIG. 2. (Color online) H dependence of M of Er_3Co at 2 K. The inset shows the $M(H)$ isotherms collected at 10, 18, 26, 38, and 46 K.

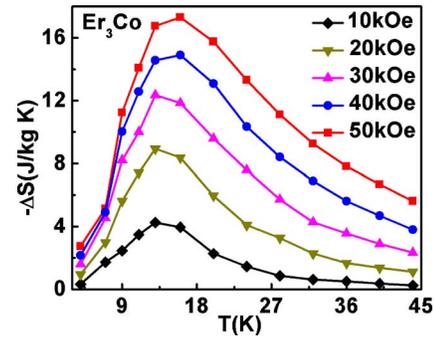


FIG. 3. (Color online) T variation of isothermal entropy change ΔS_M of Er_3Co , calculated for various field changes (ΔH) between 10 and 50 kOe.

$$\Delta S_M(T_{\text{av}}, H) = \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right) dH \approx \frac{1}{\Delta T} \int_{H_i}^{H_f} [M(T_{i+1}, H) - M(T_i, H)] dH. \quad (1)$$

Here, $T_{\text{av}} = (T_{i+1} + T_i)/2$ is the average temperature and $\Delta T = T_{i+1} - T_i$ stands for the temperature difference between two magnetization isotherms measured at T_{i+1} and T_i with the magnetic field changing from H_i to H_f . Figure 3 shows the temperature dependencies of ΔS_M of Er_3Co for various field changes (ΔH). It may be seen from Fig. 3 that, in accord with the second order character of the magnetic transition at the magnetic ordering temperature (T_{ord}), the ΔS_M versus T plots of Er_3Co are symmetric with the peak center near the T_{ord} . For $\Delta H = 20$ and 50 kOe, the maximum value of ΔS_M (ΔS_M^{max}) is found to be 9 and 17 J/kg K, respectively. It may also be noted from the ΔS_M versus T plots that the ΔS_M does not die out even at temperature well above the T_{ord} . This may be attributed to the short range magnetic correlations possibly associated with spin fluctuations arising from partial polarization of the conduction band mentioned earlier. The influence of such spin fluctuations on MCE has been reported in other intermetallic compounds as well.^{22,23} It is interesting to note that for $\Delta H = 50$ kOe, the ΔS_M^{max} values for some of the best known magnetic refrigerant materials such as ErGa, PrCo_2B_2 , DySb, HoNiAl, DyNi₂, and TbCoC₂, which have the magnetic ordering temperatures comparable to that of Er_3Co , are 21.3, 8.1, 15.8, 23.6, 21.3, and 15.3 J/kg K, respectively.^{1,3,22,24–27} Thus, the ΔS_M^{max} value of Er_3Co compares well with many known refrigerant materials studied so far. Another important quality factor of a potential refrigerant material is the refrigerant capacity or the relative cooling power (RCP). The RCP is defined as the product of maximum value of ΔS_M and the full width at half maximum of the ΔS_M versus T plot and is a measure of the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle.²² For $\Delta H = 20$ and 50 kOe, the RCP values of Er_3Co are 140 and 450 J/kg, respectively. The RCP values of potential materials such as ErGa, HoNiAl, and TbCoC₂ are 494, 500, and 354 J/kg, respectively.^{22,24,27} Thus, the RCP of Er_3Co compares well with that of many potential materials. Large MCE and RCP values along with the fact that Er_3Co is a soft ferromagnet are advantageous for magnetic refrigeration applications.^{1,3}

It was found that the ΔS_M of compound under investiga-

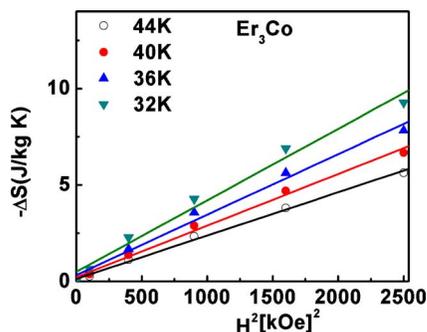


FIG. 4. (Color online) Variation of isothermal magnetic entropy change (ΔS_M) as a function of H^2 in Er_3Co at temperatures above the ordering temperature.

tions does not die out even at temperatures well above T_{ord} , possibly due to the presence of spin fluctuations. It is well known that for the compounds having spin fluctuations, ΔS_M exhibits a quadratic dependence on the field.^{6,7,23} Thus, in order to understand the origin of considerable MCE at temperatures above T_{ord} , we have plotted the above T_{ord} ΔS_M of Er_3Co as a function of H^2 (Fig. 4). We note that at temperatures above T_{ord} , the ΔS_M possesses quadratic dependence on H and, thus, confirms that in this temperature regime, the MCE of Er_3Co is governed by spin fluctuations. Similar influence of spin fluctuations on MCE has been reported in other intermetallic compounds as well.^{5-7,23,24} The presence of spin fluctuations in R_3Co compounds have also been reported independently by Baranov *et al.*²⁸ and Tripathy *et al.*⁵

IV. CONCLUSIONS

In conclusion, we have studied the magnetic and magnetocaloric properties of Er_3Co . The magnetization data reveal that the Co sublattice is nearly nonmagnetic. For field changes of 20 and 50 kOe, the isothermal entropy change in Er_3Co is found to be 9 and 70 J/kg K, which is comparable to that of many potential refrigerant materials. The MCE in paramagnetic state is found to be governed by spin fluctuations. The lack of hysteresis in magnetization isotherms and high values of isothermal magnetic entropy change and RCP make this compound a promising candidate as a low temperature magnetic refrigerant.

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