A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

LA-UR--83-2890

DE84 001685

TITLE: LOW-HYSTERESIS MATERIALS FOR MAGNETIC REFRIGERATION:

AUTHOR(S): C. B. Zimm, J. A. Barclay, and W. R. Johanson

NOTICE
PORTIONS OF THIS REPORT ARE ILLEGIBLE.
 It has been reproduced from the best available copy to permit the broadest possible availability.

SUBMITTED TO: Magnetism and Magnetic Materials Conference, November 10, 1983
 Pittsburgh, PA

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

MASTER
Los Alamos Los Alamos National Laboratory
 Los Alamos, New Mexico 87545

LOW HYSTERESIS MATERIALS FOR MAGNETIC REFRIGERATION: $\text{Gd}_{1-x}\text{Er}_x\text{Al}_2^*$

C. B. Zimm and J. A. Barclay

Los Alamos National Laboratory

Los Alamos, NM 87545

and

W. R. Johanson

Department of Physics and Astronomy

Pomona College, Claremont, CA 91711

The series of ferromagnetic intermetallics $\text{Gd}_{1-x}\text{Er}_x\text{Al}_2$ are candidate working materials for magnetic refrigeration because of their large moment, small anisotropy, and the fact that their Curie temperatures span the range 14 K to 164 K. We have measured the magnitude of the magnetic hysteresis as a function of temperature from 4 K to T_c for polycrystalline samples of these materials via AC magnetic susceptibility and magnetization hysteresis loops. We found, as expected, virtually no hysteresis in GdAl_2 , and more surprisingly, less than 3000 A/m hysteresis in ErAl_2 , and 2×10^4 A/m in $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$. Moreover, the hysteresis in $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ was ≤ 100 A/m for $T - T_c < 20$ K.

*Work performed under the auspices of the U.S. Department of Energy.

I. INTRODUCTION

Magnetic refrigeration depends on the magnetocaloric effect to produce refrigeration by execution of a thermodynamic cycle. Such refrigerators present a unique set of requirements for the magnetic refrigerant. Above about 20 K, ferromagnets with large magnetic moments must be used as working materials. Because the magnetocaloric effect is useful only over a range of 20 to 30 K on both sides of the Curie point, the Curie point of the material used in each stage of the refrigerator must match the operating temperature of that stage. The magnetic transition in the material must also be sharp, else the cooling would be small at any given temperature. The concentration of the magnetic species must be high enough that the lattice specific heat does not dilute the cooling. Moreover, the spin quantum number must be high, since the total entropy available for cooling upon demagnetization is $R \ln (2J + 1)$. Lastly, the material must be magnetically soft, i.e., relatively free of hysteresis, to allow magnetization and demagnetization without irreversible entropy production.

The cubic Laves-phase² series $\text{Gd}_{1-x}\text{Er}_x\text{Al}_2$ is ferromagnetic throughout its composition range, with the Curie temperature changing continuously from about 165 K for GdAl_2 to 15 K for ErAl_2 .³ The magnetic moment per rare earth (RE) ion in the ferromagnetic state is also large⁴ (about 7 Bohr magnetons) throughout the composition range. Hence, these materials are candidates for use in a multistage magnetic refrigerator. Although one would expect little hysteresis for the S-state configuration of gadolinium in GdAl_2 (although a relatively weak magneto-crystalline anisotropy is observed⁵), the orbital angular momentum of the erbium ion in ErAl_2 leads to substantial magneto-crystalline anisotropy,⁵ and hence, possibly to hysteresis. This paper reports our investigation of hysteresis in GdAl_2 , ErAl_2 , and $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ by AC susceptibility and DC magnetization experiments.

II. EXPERIMENTAL METHOD

Polycrystalline samples of GdAl_2 , ErAl_2 , and $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ were prepared by Ames Labs by melting of 99.9% RE and 99.999% Al in an argon arc furnace. Cast cylindrical samples whose demagnetizing factors ranged from 0.04 to 0.02 (MKS) were used for susceptibility experiments. Small needle-shaped samples with demagnetizing factors of 0.03 to 0.08 were cut with a wafering saw for use in the magnetization measurements.

The differential susceptibility $\partial M / \partial H|_{H=0}$ was measured using a mutual inductance bridge. The AC field applied to the sample was 30 A/m RMS (1 Gpp) at 17 Hz. The applied field and the detected component of the susceptibility were parallel to the long axis of the cylindrical samples.

Static magnetization was measured by a PAR vibrating-sample magnetometer with a superconducting solenoid having a maximum field of 8 T. The static field was applied parallel to the long axis of the samples.

III. RESULTS

Figure 1 gives the differential magnetic susceptibility, uncorrected for demagnetization, for GdAl_2 , $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ and ErAl_2 as a function of temperature. Note that for each material, the increase in susceptibility upon cooling from the paramagnetic state to the ferromagnetic state is sudden and large, the ratio $\chi(T_C - 1 \text{ K}) / \chi(T_C + 10 \text{ K})$ being at least 50. The plotted value of χ reaches a maximum value limited by demagnetizing effects below T_C . The apparent drop in susceptibility observed for $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ below 80 K and ErAl_2 below 13 K occurs when the hysteresis becomes comparable to the small (30 A/m) AC applied field.

The static magnetizations of GdAl_2 , $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ and ErAl_2 were also measured. The zero-field, 4-K magnetizations, estimated by visually extrapolating the high field ($H = 1$ to 5×10^6 A/m) magnetization to zero field, are given in Table I. The magnetizations are consistent with those of previous authors.^{4,5,6} Symmetrical hysteresis loops were then taken using fields just sufficient to saturate the magnetization. The coercive force [$H \uparrow (M = 0) - H \downarrow (M = 0)/2$], independent of demagnetization effects, is tabulated in Table I as a function of T/T_c for the three materials. A typical hysteresis loop for $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ is shown in Fig. 2. Note that for the temperature range of interest for magnetic refrigeration, $0.7 T_c$ to $1.3 T_c$, the hysteresis is negligible for all three materials. Moreover, even at 4 K, the hysteresis observed is small compared to the $5\text{--}10 \times 10^6$ A/m fields contemplated for magnetic refrigerators.

IV. DISCUSSION

The absence of hysteresis in GdAl_2 is not surprising in light of the S-state character of the gadolinium ion. The relatively small hysteresis in ErAl_2 is more remarkable considering that the single crystal saturation magnetizations in the (111), (110), and (100) directions remain different in a field of 1.2×10^7 A/m.⁶ It may be that the 8-fold degeneracy of the (111) easy directions permitted by the cubic crystal structure prevents effective pinning of the magnetization by domain interaction effects. The enhanced hysteresis of $\text{Gd}_{0.5}\text{Er}_{0.5}\text{Al}_2$ over that of ErAl_2 probably comes from the appearance of local uniaxial anisotropy produced by the distribution of gadolinium and erbium neighbors of each RE ion, as well as by possible disordering between RE and aluminum sites.^{3,7}

The $\text{Gd}_{1-x}\text{Er}_x\text{Al}_2$ system clearly shows promise for magnetic refrigeration. The spin is large, the magnetic concentration is high, and the materials are magnetically soft. Moreover, by varying the Gd/Er ratio, the Curie point may be adjusted over a wide range, allowing optimum Curie points for each stage of a refrigerator. It must still be verified that the specific heat anomaly due to the ferromagnetic transition is sharp for the $\text{Gd}_{1-x}\text{Er}_x\text{Al}_2$ series, and that the magnetocaloric effect is indeed large. Measurements of specific heat as a function of temperature and field for $\text{Gd}_{1-x}\text{Er}_x\text{Al}_2$ are in progress.

Figure Captions

Fig. 1. AC susceptibility in zero static field, uncorrected for demagnetizing effects. The AC field applied by the mutual inductance bridge is 30 A/m RMS.

Fig. 2. Magnetization vs. internal magnetic field (H_{INT}) (corrected for demagnetization) for $Gd_{0.5}Er_{0.5}Al_2$ at half its Curie temperature.

References

1. J. A. Barclay and W. A. Steyert, Electric Power Research Institute Report, EPRI EL - 1757, April, 1981 and references therein.
2. J. H. Wernick, S. R. Haszko, and D. Dorsi, J. Phys. Chem. Solids, 23, 567 (1962).
3. A. Chelkowski, E. Talik, and G. Wnetrzak, J. Phys. F, 13, 483 (1983).
4. H. J. Williams, J. H. Wernick, E. A. Nesbitt, and R. C. Sherwood, J. Phys. Soc. Jpn., 17, Supp. B-I, 91 (1962).
5. J. Burd and E. W. Lee, J. Phys. C., 10, 4581 (1977).
6. H. G. Purwins, E. Walker, B. Barbara, M. F. Rossignol, and A. Furrer, J. Phys. C, 9, 1025 (1976).
7. D. Konopka, M. Sobaszek, and T. Rendecki, J. Less-Common Met., 81, 1 (1981).

TABLE I
Curie Temperature (T_c); Static Magnetization Extrapolated
to Zero Field (M); and Coercive Forces (H_c)

	T_c , K	$M(H \rightarrow 0)$ at 3.9 K, A/m	H_c A/m 4 K	$T_c/2$
GdAl ₂	164 $\pm$ 3	1.03 $\times 10^6$	< 200	< 200
Gd _{0.5} Er _{0.5} Al ₂	96 $\pm$ 2	1.02 $\times 10^6$	1.1 $\times 10^4$	600
ErAl ₂	14 $\pm$ 1	1.09 $\times 10^6$	1.5 $\times 10^3$	

Susceptibility, $\frac{\partial M}{\partial H}$, Arbitrary Units