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T-S diagram for gadolinium near the Curie temperature

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The magnetocaloric effect in polycrystalline Gd was measured at temperatures from 190 to 370 K in applied fields from 1 to 7 T. The magnetocaloric temperature changes were combined with existing zero-field specific heat data to construct a T-S diagram for Gd near the Curie point. Experimental values of ΔT were also compared with values calculated from a simple mean field theory, which predicts rather well both the general shape of the magnetocaloric curve and the relative magnitudes of the temperature changes in various measuring fields. The maximum ΔT with applied field was about 14 K at 7 tesla, and maxima in all applied fiels occurred near 292 K. The relatively large magnetocaloric effect in Gd near room temperature is attractive for potential magnetic refrigeration applications, and the experimental T-S diagram may now be used to refine estimates of the performance of Gd as a solid magnetic refrigerant.

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INTRODUCTION

The concept of cooling by magnetic cycling was first suggested in 1926 (Debye) and 1927 (Giauque), and extremely low cryogenic temperatures are now routinely achieved by the adiabatic demagnetization of paramagnetic spin systems. Temperature changes during the isentropic portion of a magnetic cooling cycle are described by the magnetocaloric effect:

$$dT = -(T/C_H)(\partial M/\partial T)_H \, dH \qquad (1)$$

where T is temperature (K), C_H is the heat capacity at constant field (J/mole/deg K), M is the magnetization (T), and H is the applied field (A/m or normalized to T). Recently there has been considerable interest in magnetic refrigeration at higher temperatures because of potential advantages which include thermodynamic efficiencies close to the Carnot efficiency (1). In this experiment, the magnetocaloric effect in Gd was measured and combined with existing zero-field heat capacity data to generate a T-S diagram which can be used to evaluate Gd as a magnetic refrigerant.

Cooling by paramagnetic demagnetization is inadequate above cryogenic temperatures because the heat capacity of the working material is too large to permit a significant temperature change with the magnetic entropy absorbed during demagnetization. In order to realize an appreciable temperature change near liquid nitrogen or room temperatures, magnetic materials with a large magnetic entropy "reservoir" must be used at temperatures near which an applied field adequately changes the level of the reservoir. Ideal candidates include ferromagnetic materials with Curie points in the temperature range of the cooling cycle. The ferromagnetic Curie point of Gd is near room temperature (∿292 K). Gd has a moderately high J value (7/2) and, therefore, has a substantial magnetic entropy reservoir near the Curie point. In addition, Gd can be formed into thin sheets for optimal thermal exchange in refrigerator applications, and alloys of Gd with Dy or other rare earths exhibit a wide range of Curie and Neel temperatures which may meet specific application requirements. Because of these properties, Gd or Gd alloys might be used for magnetic refrigeration to the ice point or, as the first stage in a multiple stage cycle, to LN_2 temperatures and below.

The magnetocaloric effect in Gd measured at 7 T between 160 and 340 K has been reported previously, as well as a comparison with mean field theory (MFT) calculations (2). MFT describes the magnetic behavior of most ferromagnetic materials far above the Curie temperature, but MFT and improvements of this theory have so far proved inadequate for predicting state variables, such as entropy, near T_C. The magnetocaloric measurements and experimental entropies presented here for applied fields from 1 to 7 T between 190 and 370 K may now provide the basis for evaluating Gd as a magnetic refrigerant in fields achievable with permanent magnets (∿1 T).

EXPERIMENT

Fig. 1 shows the magnetocaloric effect measurement apparatus. A simple vacuum chamber (a) was constructed from standard copper tubing and fittings, and enclosed in styrofoam for conductive thermal shielding. Teflon plugs at the top and bottom of the chamger (b) insulated the sample from the can and held the sample firmly against strong magnetic forces which might develop if the sample is not centered in the solenoid. A single layer of aluminized mylar loosely wrapped around the sample support system (c) reduced radiative

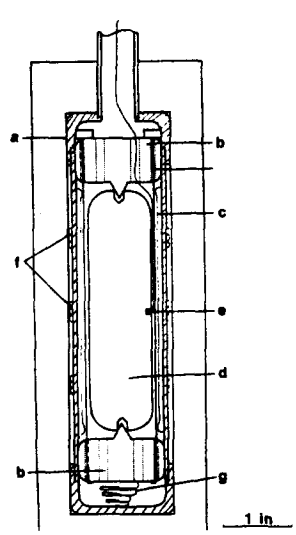

Fig. 1. Sample support system; (a) copper can, (b) teflon plugs, (c) radiation shield, (d) Gd sample, (e) thermocouple, (f) heater, (g) nonmagnetic spring.

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coupling with the can. The 3.5 in. long x 0.9 in. dia. Gd sample (d) was cut from a cast cylindrical, polycrystalline ingot and machined smooth with hemispherical ends to approximate an ellipsoid. A brazed type T thermocouple (#32 awg Cu, #28 awg Cn) was imbedded with epoxy in a small drilled cavity near the midplane of the sample (e). The thermocouple and the cavity were kept small to improve thermal response. A second thermocouple recorded the can temperature for comparison with the sample temperature

Magnetic fields up to 7 T were generated by a water cooled, 2½ in. clear bore solenoid. The field was uniform to within ± 1% over the length of the sample. During the experiment, the field was ramped at about 1 T/s to the desired value, held for up to 60 s, and then reduced at the same rapid rate. The field was maintained for a time which was long compared with the thermal response of the thermocouple and short compared with the thermal diffusion time along the length of the sample. Temperature changes were recorded with a standard chart recorder, and the magnetocaloric ΔT's were determined by a subtraction of baseline and high field values near the center of the time interval. The temperature changes appeared to be reversible. Heating and cooling between measurements were accomplished by controlling the temperature of the can, sometimes in conjunction with temporarily admitting a small amount of exchange gas into the can. A 10 watt heater wrapped around the can (f) provided heating, and dipping the can and styrofoam jacket into LN_2 provided rapid cooling. The sample could then be cooled or heated rapidly by admitting and then pumping out the exchange gas, or more slowly by radiation (and some conduction). Magnetocaloric measurements were taken when the sample and the can were nearly in thermal equilibrium.

The major sources of error were baseline drift from nonadiabatic conditions and slow thermocouple response time. Thermal drift arises because of the simplicity of the vacuum and shielding systems, and the slow thermocouple response was caused primarily by the epoxy selected. Use of a dewar significantely improves thermal shielding (3), but equilibrium times become longer and the bulk of the apparatus may be a problem in smaller magnet bores. Temperature drift rates were generally less than 0.3 K/min. when the sample and can temperatures were kept nearly the same, however the maximum ΔT of up to 14 K in the Gd sample disrupted radiative equilibrium near the Curie point. Graphical extrapolation methods for determining ΔT were especially inaccurate in this temperature range. Reproducibility of the data is estimated to be within about 3% over most of the temperature range.

RESULTS AND DISCUSSION

The magnetocaloric data for polycrystalline Gd in applied fields of 1, 3, 5, and 7 T is shown in Fig. 2. The maximum temperature change occurred at about 292.5 K in all applied fields, and the values of ΔT at the Curie point were 3.6 K (1 T), 7.8 K (3 T), 11.0 K (5 T), and 13.8 K (7 T). The magnetocaloric temperature change falls to half of the maximum value at both higher and lower temperatures within ± 40 K of T_C. The general shape of these curves may be understood by referring to Eq. 1 and Fig. 3. From Eq. 1, the magnetocaloric effect is greatest when $(\partial M/\partial T)_H$ is large over the interval dH. A plot of M(T)/M(0) derived from a standard MFT calculation is shown in Fig. 3. An inflection point occurs near the temperature chosen as the Curie point (here taken to be the observed ferromagnetic Curie point of 292 K). Because the slope $(\partial M/\partial T)_H$ peaks near T_C at all fields, the magnetocaloric data also peaks near T_C as in the superimposed 7 T data (unscaled). At low temperatures (near 200 K), the sample approaches magnetic saturation, and application of a magnetic field does not change the magnetic entropy enough to appreciably heat or cool the sample. At higher temperatures (near 380 K), the applied field becomes less effective in producing magnetic order.

Similar MFT calculations were made to predict the magnitude of the magnetocaloric temperature changes at the experimental applied fields for comparison with the data. These calculated ΔT's are shown as solid curves in Fig. 2. The method used to calculate ΔT(H,T) has been described previously and involves an iterative fit of the initial and final total entropies by variation of ΔT (2). At the initial and final temperatures,

$$S = S(\text{lattice}) + S(\text{electronic}) + S(\text{magnetic}) \quad (2)$$

where S(lattice) is calculated using a Debye lattice heat capacity (Θ_D= 172 K), S(electronic) is taken as the average value of La and Lu (2.6 x 10^{-3} cal/mole/K), and the magnetic entropy is calculated from MFT (4,5,6). The paramagnetic Curie temperature for polycrystalline Gd (310 K) was chosen as the Curie temperature which

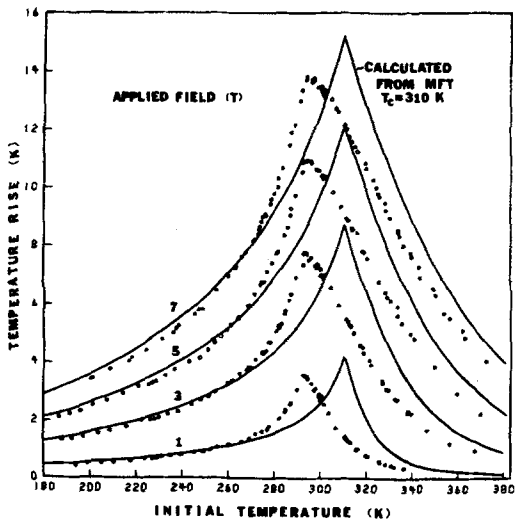

Fig. 2. Adiabatic temperature change vs. temperature for various applied fields in polycrystalline gadolinium.

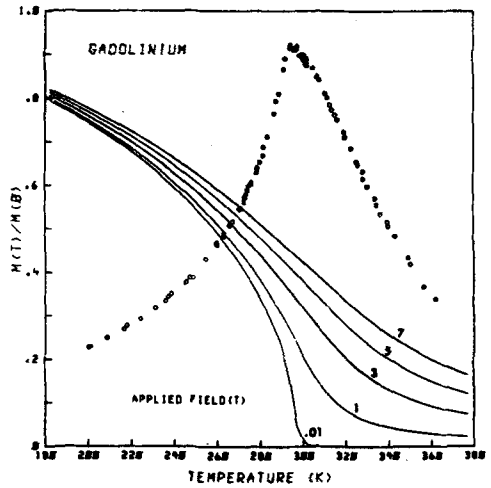

Fig. 3. Mean field theory calculation of the relative magnetization in gadolinium vs. temperature; the magnetocaloric effect at 7 T (unscaled) is superimposed.

Table I. Polynomial coefficients for entropy curves.

$$S = a_o + a_1T + a_2T^2 + a_3T^3$$

Applied Field (T)	Temperature Range (K)	a_o	a_1	a_2	a_3
1	194 to 300	-.69072E+00	.96923E-01	-.21608E-03	.26888E-06
1	300 to 333	-.70544E+02	.71925E+00	-.20181E-02	.19478E-05
3	189 to 305	.31537E+00	.82246E-01	-.14664E-03	.15721E-06
3	305 to 368	-.26763E+02	.30337E+00	-.71476E-03	.59690E-06
5	189 to 308	.51231E+00	.78999E-01	-.13050E-03	.12804E-06
5	308 to 372	-.84158E+01	.13886E+00	-.23036E-03	.12665E-06
7	204 to 310	.10111E+01	.72761E-01	-.10546E-03	.92132E-07
7	310 to 376	.39061E+01	.30013E-01	.84879E-04	-.17440E-06

would best describe the experimental results well away from the Curie point (7). On the basis of the comparison in Fig. 2, MFT appears to predict remarkably well the maximum ΔT's and the lower temperature data, despite the simplfying assumptions inherent in the theory. Near the ferromagnetic Curie temperature, disagreement is expected because of the onset of clustering. At higher temperatures, the theoretical and experimental points appear to be approaching agreement. Better agreement might also be expected at the lower temperatures if the data were corrected for demagnetization. The geometrical demagnetization factor is about 0.05 (8). At 200 K, M may reach nearly 0.8 M(0) or about 19 T, and the demagnetization field may be as high as 0.1 T. In this temperature range, the theoretical curve should be shifted slightly downward to reflect the geometrical demagnetization correction.

The zero-field heat capacity data of Griffel et. al. (9) was used to calculate the zero-field entropy of Gd. Magnetocaloric temperature shifts were then added to each (T,S) point at constant entropy to generate a set of (T_{new},S points for each applied field. Fig. 4 shows the resulting T-S diagram for Gd over the entire measuring temperature and applied field rantes. Fig. 5 shows the same data over a more limited temperature range near T_C. The cusp in the zero-field entropy reflects the discontinuity in the zero-field heat capacity data at T_C= 291.6 K exhibited by Griffel's sample of Gd. A magnetic field should remove the cusp, because application of a magnetic field removes the discontinuity in the heat capacity. However, a slight discontinuity of slope remains in the data derived from magnetocaloric measurements because of differences in the two samples, neglect of demagnetization factors, and experimental uncertainty. Table I contains third order polynomial regression coefficients for each entropy curve in the temperature regions above and below this slight discontinuity. Agreement with the experimental points is ± 0.005 cal/mole/deg K.

From the T-S diagram it may be seen that an isothermal change of magnetic field from 0 to 7 T near the Curie point generates an entropy change of about 0.5 cal/mole/deg K and a corrosponding heat "pumping" capacity of about 150 cal/mole. At 1 T, this value is reduced to about 30 cal/mole per cycle. However, even at this lower value, Gd compares favorably with more commonly used refrigerants and shows significant promise as a solid magnetic refrigerant.

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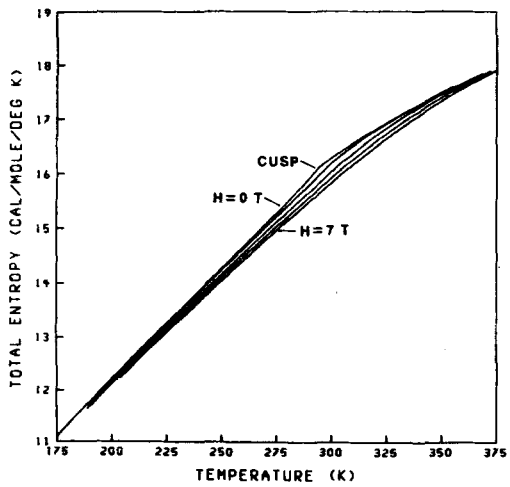

Fig. 4 Entropy vs. temperature of gadolinium for various applied fields; entropy values were calculated from the zero-field heat capacity data of Griffel et. al. (9) and the magnetocaloric data.

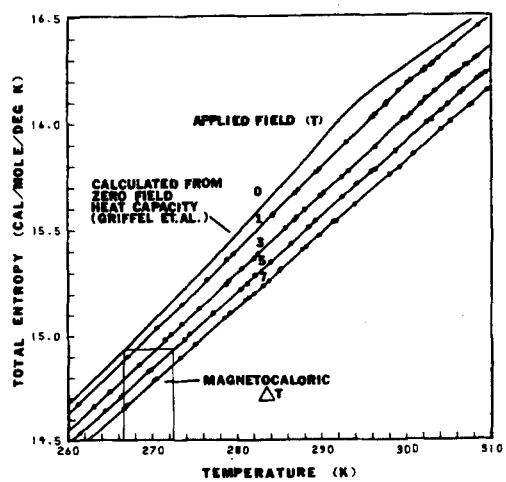

Fig. 5. Entropy vs. temperature of gadolinium near the Curie point.