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SUITABILITY OF THE RARE-EARTH COMPOUNDS
Dy$_2$Ti$_2$O$_7$ AND Gd$_3$Al$_5$O$_{12}$ FOR LOW TEMPERATURE
(4K-20K) MAGNETIC REFRIGERATION CYCLE

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ABSTRACT

Measurements have been made of the magnetic entropy and magnetization of powered samples of the compounds $Dy_2Ti_2O_7$ and $Gd_3Al_5O_{12}$. The magnetization has been measured for temperatures at and below 4.2 K, in applied fields ranging to 7.0 tesla. Isothermal changes in magnetic entropy have been measured for temperatures from 1.2 to 20 K, in applied fields up to 10 tesla. The results of the measurements are consistent with a doublet ground state for $Dy_2Ti_2O_7$, and an eight-fold degenerate ground state for $Gd_3Al_5O_{12}$. Absolute values of magnetic entropy have been obtained at the lower temperatures, permitting the isotherms to be properly located in the S-H plane with the use of adiabatic magnetization data. The iso-field lines in the S-T plane have been determined. The results indicate that $Dy_2Ti_2O_7$ can absorb a maximum of 71±4 joules/kg of heat at 4.2 K, while $Gd_3Al_5O_{12}$ can absorb 233±11 joules/kg at the same temperature. The large difference between the two is most likely a result of crystal field interactions in the dysoprosium compound. Both materials can be cycled adiabatically between 4.2 and 20 K.

INTRODUCTION

The practical use of superconducting material in technological areas such as power generation and transmission will depend on the development of an efficient means of refrigeration. The Lewis Research Center is investigating the feasibility of magnetic cooling (ref. 1) at

temperatures above 4.2 K, with initial emphasis on the range from boiling liquid helium (~4.2 K) to boiling liquid hydrogen (~20 K). The investigation has centered on various compounds of the rare-earths because of the wide variability of their magnetic properties. In order to determine the suitability of any particular material for use in such a refrigeration cycle two quantities are measured - magnetization, and magnetic entropy. The magnetization is measured by integrating the difference voltage produced by two search coils, one of which contains the sample, as the magnetic field is swept at a constant rate. Magnetic entropy changes are determined by integrating the power required to keep the sample at a constant temperature as the magnetic field is either increased or decreased. $Dy_2Ti_2O_7$ and $Gd_3Al_5O_{12}$ are the first materials for which the measurements have been made.

RESULTS & DISCUSSION

Figure 1 shows the magnetization of $Dy_2Ti_2O_7$ as a function of applied field for several temperatures in the liquid helium range. The susceptibility, as determined by the initial slopes of these curves, yields an effective moment of 9.6+.4 Bohr magnetons per ion, which is within about 10% of the free ion value of 10.63. The saturation region, however, indicates only 4.7+.2 Bohr magnetons per ion, and exhibits a temperature independent van-Vleck paramagnetism as well. The discrepancy can be resolved by assuming that the crystalline electric fields produced by neighboring oxygen atoms have perturbed the magnetic energy levels, leaving only a doublet ground state consisting of the two $J_z = \pm 15/2$ levels. The van-Vleck paramagnetism is the result of a slight perturbation of the ground state by a nearby upper level which was also originally part of the $J = 15/2$, 16-fold degenerate ground state of the free Dy^{+++} ion.

Figure 2 shows the magnetization of $Gd_3Al_5O_{12}$ as a function of applied field for two different temperatures. In this case the saturation magnetization yields 6.8 ± 0.3 Bohr magnetons per ion, which agrees within experimental error with the free-ion value of 7. This result is to be expected because the orbital angular momentum of the Gd^{+++} ion

is zero, so that crystal fields, which act principally on the orbital moment, cannot perturb the ground state energy levels to any extent.

Figure 3 shows the variation of the magnetic entropy of $Dy_2Ti_2O_7$ with applied field for several temperatures. The isotherms were located in the S-H plane by adiabatically magnetizing the sample in a separate experiment from one of the lower temperatures, where the absolute change in magnetic entropy was known. The temperatures reached as the field was swept are shown by the dashed line, which is corrected for the lattice entropy. The value of the lattice specific heat constant used was that reported by van Guens (ref. 2), $a = 2.2 \times 10^{-6}$ joules/gm deg^4. From this information the isofield lines in the T-S plane can be constructed, and the results are shown in figure 4. The maximum zero-field entropy for this compound is expected to be 0.0216 joule/gm-deg. The total entropy available at 4.2 K is just 0.017 joule/gm-deg, and the correspinding amount of heat that can be absorbed in a demagnetization from even an infinite magnetic field is approximately 71 joules/kg. One possible refrigeration cycle between 4 and 20 K for this compound is outlined by the dashed lines connecting points a, b, c, d. A maximum cooling capacity of appriximately 31 joules/kg per cycle can be obtained with these operating temperatures.

The magnetic ordering temperature for $Gd_3Al_5O_{12}$ was determined from the data shown in figure 5 to be near 3.3 K. Below about 3.3 K the sample initially absorbs heat with increasing field, indicating that the sample is trying to cool, rather than heat. Above 3.3 K heat is rejected from the sample as the field is increased. This kind of behavior is somewhat surprising although it has been observed for some rare-earth iron garnets (ref. 3). In the iron garnets the rare-earth ions order in the presence of the exchange field produced by the Fe ions. The alignment between rare-earth and Fe ions sublattices is antiparallel. When an external field is applied, the Fe ions align with the field, and the rare-earth ions are antiparallel to it. As the external field increases it diminishes the effect of the Fe exchange field on the rare-earth sublattice, causing it to become disordered. The observation of an initial cooling in the aluminum garnet suggests that there are two inequivalent

rare-earth sublattices aligned antiparallel to one another. Further exper-
imental evidence is needed to clarify the situation. The essential point is
that there is apparently a magnetic ordering temperature near 3.3 K.

Figure 6 contains several of the isotherms in the S-H plane for
$Gd_3Al_5O_{12}$, again with the path of an adiabatic magnetization shown by
the dashed curve. In this case it was assumed that the zero-field entropy
at 12, 16 and 20 K would be equal to the maximum value, 0.065 j/gm K,
since they are well above the magnetic ordering temperature mentioned
previously. The entropy differences at those fields and temperatures
were than used to calculate the lattice specific heat constant, giving a
value of $1.3 \pm 0.1 \times 10^{-6}$ joule/gm K^4. This value was used to calculate
various entropy values on the 4.2 K isotherm. The predicted and
observed values agreed to within 3% of one another.

A portion of the T-S plane for $Gd_3Al_5O_{12}$, constructed from the
data of figure 6 is shown in figure 7. A cycle operating between 4.2 and
20 K, and 0 - 10 tesla has been sketched in the figure. Although the
entropy available at 4.2 K is over 3 times that of the dysprosium com-
pound, the entropy available per cycle is still about the same. Hence
one would expect a cooling capacity of about 31 joules/kg for this com-
pound as well. The maximum amoung of heat that can be absorbed by
$Gd_3Al_5O_{12}$ at 4.2 K during a demagnetization from an infinite magnetic
field is, however, 233 joules/kg.

CONCLUSION

The results presented here indicate that a magnetic refrigeration
cycle operating between boiling liquid helium (4.2 K) and boiling liquid
hydrogen (20 K) is a possibility. The two compounds studied so far could
conceivably be used to produce a refrigerator with a cooling capacity
ranging from a few tenths of a watt to a few watts per kilogram of "working
substance", assuming cycling times ranging from a few minutes to a
few seconds.

REFERENCES

1. G. V. Brown, National Aeronautics and Space Administration Report No. TM-X-52983, 1971.

2. J. R. van Geunes, thesis (University of Leiden, 1966).

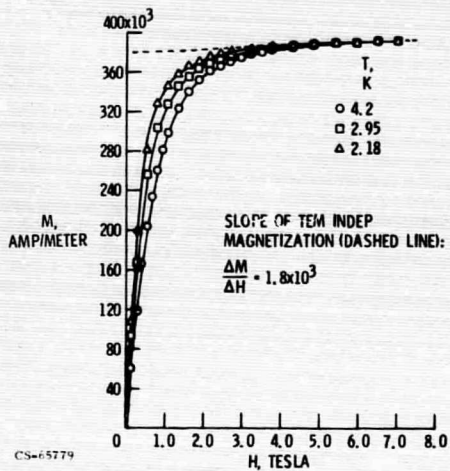3. A. E. Clark, and R. S. Alben, J. Appl. Phys. 41, 1195 (1970).

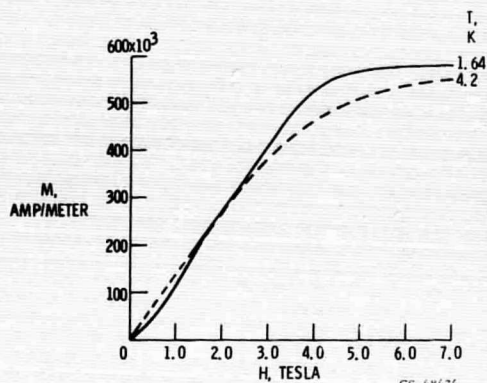Figure 1. - Magnetization versus applied field for Dy$_2$Ti$_2$O$_7$.

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SLOPE OF TEM INDEP MAGNETIZATION (DASHED LINE):

$$\frac{\Delta M}{\Delta H} = 1.8 \times 10^3$$

T, K
○ 4.2
□ 2.95
△ 2.18

M, AMP/METER

H, TESLA

Figure 2. - Magnetization versus applied field for Gd$_3$Al$_5$O$_{12}$.

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T, K
1.64
4.2

M, AMP/METER

H, TESLA
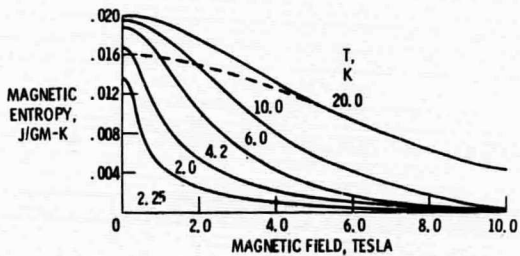
Figure 3. - S-H plane for Dy$_2$Ti$_2$O$_7$.

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MAGNETIC ENTROPY, J/GM-K

MAGNETIC FIELD, TESLA

T, K
20.0
10.0
6.0
4.2
2.0
2.25
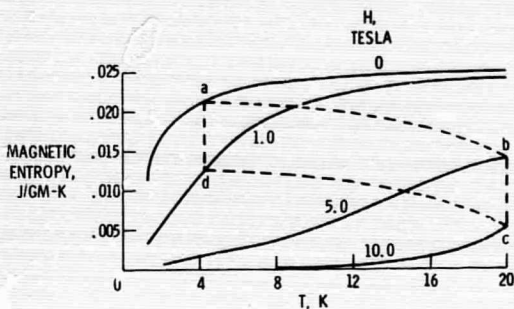
Figure 4. - Magnetic entropy-temperature plane for Dy$_2$Ti$_2$O$_7$.
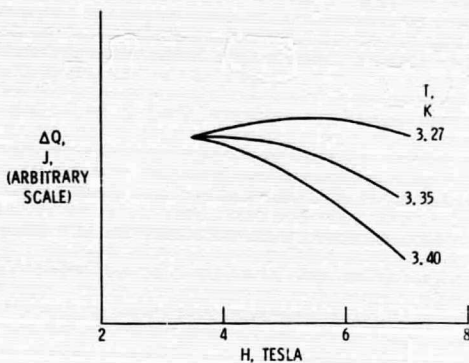

Figure 5. - Variation of heat adsorbed by sample as applied field is increased. (Remnant field of solenoid used is 3.5 T.) Scale of ordinate is arbitrary.
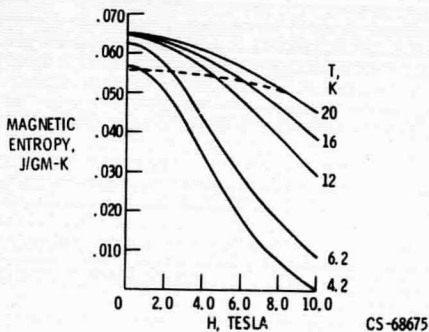

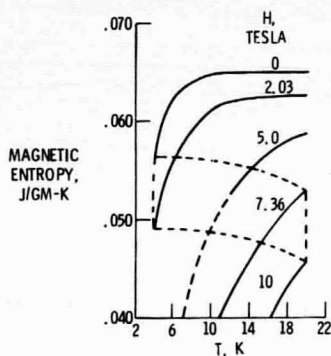Figure 6. - S-H plane for Gd$_3$Al$_5$O$_{12}$.

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Figure 7. - Magnetic entropy - temperature plane for Gd$_3$Al$_5$O$_{12}$.

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