about 10^{15} per cm^3, ionized impurity scattering slightly dominates for zero magnetic field and for temperatures around 30°K, but that at high magnetic fields the acoustic scattering is predominant. The curves of Love and Wei for the doped sample appear to agree with this. The curves are similar to those for the pure samples except that the resistivity ratio is cut down by a factor due to the higher resistivity at zero field. Since no samples had a high enough impurity concentration to make ionized impurity scattering predominant at high fields, no experimental curves are drawn in Fig. 2.

In the limit of very high magnetic fields $\rho(H)/\rho(0)$ for ionized impurity scattering saturates. This is seen for the ⟨110⟩ direction from Eq. (49) in which $C-1$ and λ^2 are both proportional to $1/H$. More accurate expressions for τ for the other directions, similar to Eq. (47) for the ⟨110⟩ direction, would lead to saturation for these directions also. In Fig. 2 there is already saturation in the ⟨110⟩ direction and with only slightly higher fields there will be saturation in the ⟨111⟩ direction. The saturation in the ⟨100⟩ direction will not occur until the magnetic field is four or five times as large, so there is a considerable range in which there is a linear change with H. $\rho(H)/\rho(0)$ is approximately a function of H/T so this saturation occurs at higher fields for higher temperatures.

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Adiabatic Demagnetization with Yttrium-Rare Earth Alloys*

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Alloys of yttrium with 0.3 and 1.0 atomic percent gadolinium, 1.0 at. % dysprosium, and 0.6 and 1.0 at. % holmium have been investigated to determine their usefulness as the working substance for adiabatic demagnetization. In addition, single crystals of 0.6 and 1.0 at. % holmium-yttrium alloys were studied. Those alloys which exhibited paramagnetic susceptibility behavior in the temperature range 1.2–4.2°K were demagnetized adiabatically from about 11 koe and 1.25°K. The lowest temperature attained was 0.76°K for the single crystal of 1.0 at. % holmium with the magnetic field parallel to the a axis of the hexagonal crystal. Magnetization measurements obtained for the single crystals in the temperature range 1.2–4.2°K indicated strong anisotropy with the a axis as the easy axis of magnetization. Hysteresis was observed in the magnetization of the 1.0 at. % holmium single crystal with the a axis parallel to the field. Entropy removal during magnetization was calculated from the magnetization data for the single crystals and found to be only about 15% of that expected if the alloy behaved like an ideal paramagnetic substance.

INTRODUCTION

THE use of thorium-dysprosium metal alloys in magnetic cooling to obtain temperatures less than 1°K has recently been reported by Parks and Little.[1] We report here the results of adiabatic demagnetizations and susceptibility and magnetization measurements on dilute alloys of rare-earth metals in yttrium.

The work was initiated because of the thermal-contact advantages metal alloys would have over conventional salts. Normally with a metal, one might expect eddy-current heating when demagnetizing, but the high residual resistivities of our alloys essentially eliminate this problem. Yttrium was chosen as the host metal since it has the same crystal structure and very nearly the same lattice parameters as the solute metals. Gadolinium ($J=S=7/2$), with no orbital moment and 7 unpaired spins, was the first solute metal used. In order to study the effect of the spin of the solute metal on the Curie (or Néel) temperature, dysprosium ($J=15/2$, $S=5/2$) and holmium ($J=8$, $S=2$) alloys were next investigated. The small cooling effect observed during adiabatic demagnetization of the holmium-yttrium alloys prompted a study of the magnetic properties of single crystals of these alloys.

MATERIALS STUDIED

The pure metals used in fabrication of the alloys were prepared in this laboratory by methods previously reported.[2,3] The alloys were made by arc melting together in a helium atmosphere the proper amounts of the constituent metals. The button formed by this process was turned over and remelted several times in order to insure a homogeneous alloy. The samples were shaped by machining on a lathe into the nominal size of 1.5-in. length, by 0.6-in. diam. The alloys investigated consisted of two gadolinium-yttrium alloys with 0.3

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† Present address: Department of Physics, Luther College, Decorah, Iowa.
[1] R. D. Parks and W. A. Little, *Seventh International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, Canada, 1960), Official Programme, 354–356.
[2] F. H. Spedding and A. H. Daane, J. Am. Chem. Soc. **74**, 2783 (1953).
[3] C. V. Banks, O. N. Carlson, A. H. Daane, V. A. Fassel, R. W. Fisher, E. H. Olson, J. E. Powell, and F. H. Spedding, Atomic Energy Commission Report IS-1, Iowa State University, Ames, Iowa, 1959 (unpublished).

TABLE I. Spectrographic analysis of yttrium host metal for the various alloys.

Element	Impurity in yttrium (ppm) Gd-Y alloys	Dy-Y alloys	Ho-Y alloys
C	120	63	89
N	160	60	20
F	1180	72	71
O	1300	425	200
Ta	<100	<100	100
Ti	<50	<50	<50
Ni	200	200	200
Mg	<15	<15	<15
Fe	200	200	200
Ca	<10	<10	<10

and 1.0 at. % Gd, one dysprosium-yttrium alloy with 1.0 at. % Dy, and two holmium-yttrium alloys with 0.6 and 1.0 at. % Ho. A spectrographic analysis was made on the yttrium metal used in each alloy. The results are shown in Table I.

Single crystals were obtained for two alloys of holmium-yttrium using a grain-growth technique that has been described by Hall *et al.*[4] The crystals were formed into rectangular parallelepipeds by grinding and polishing on emery paper. The crystal dimensions were 3×5×6 mm for the 0.6 at. % Ho alloy and 3×3×9 mm for the 1.0 at. % Ho alloy.

EXPERIMENTAL PROCEDURE

The magnetic susceptibility of the polycrystalline alloy samples was measured for temperatures below 4.2°K. A dc ballistic method,[5] for which the susceptibility was proportional to the throw of a galvanometer, was used for these measurements. Absolute susceptibilities were obtained by calibrating the system with a compressed pill of iron ammonium alum of the same shape and size as the sample. Temperatures in the range 1.2–4.2°K were obtained from the liquid-helium bath using the 1958 scale.[6] Measurements below 1.2°K for the 0.3 at. % Gd alloy were obtained by adiabatic demagnetization of the alloy, and for the 1.0 at. % Ho alloy by cooling with a demagnetized paramagnetic salt pill. Temperatures below 1.2°K for the 0.3 at. % Gd alloy were measured with a calibrated carbon resistor, and for the 1.0 at. % Ho alloy were determined from the Curie temperature of the salt pill.

Magnetization measurements in the temperature range 1.4–4.2°K were made on the single crystals of 0.6 at. % Ho and 1.0 at. % Ho alloy. (Measurements with the *a* axis parallel to the field were made at several temperatures in this range. Measurements with the *c* axis parallel to the field were made only at 4.2°K, since it was not possible to maintain the *c* axis parallel to the field at lower temperatures due to the strong anisotropy.) The measurements were made with a 3-kw Weiss-type magnet that produced a uniform field gradient in the vertical direction for fields of zero to 11 koe. A line drawing of the apparatus is shown in Fig. 1. The sample was attached to a copper sample holder (not shown), which in turn was suspended from an analytical balance at the end of a long thin quartz rod. The liquid-helium cryostat was of standard design; bath temperature was lowered by reducing the pressure over the liquid helium. Thermal contact between the sample

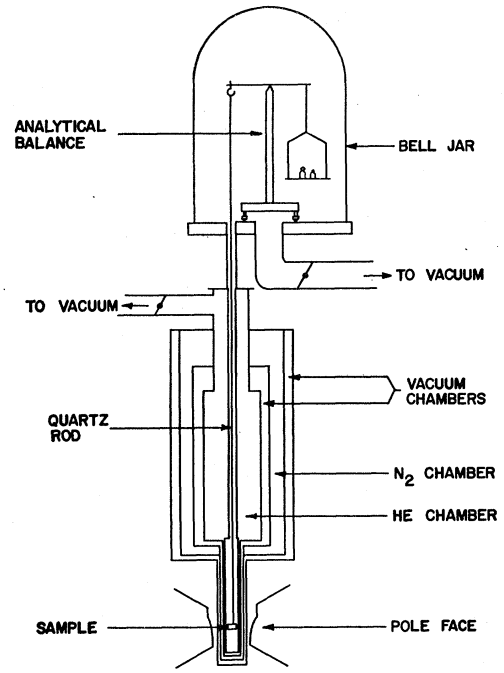

FIG. 1. Apparatus for magnetization measurement. The sample was suspended from the balance at the end of a long quartz rod. The pole faces were cut hyperbolically to give a uniform vertical field gradient. Helium exchange gas in the sample tube maintained the sample at the temperature of the liquid-helium bath.

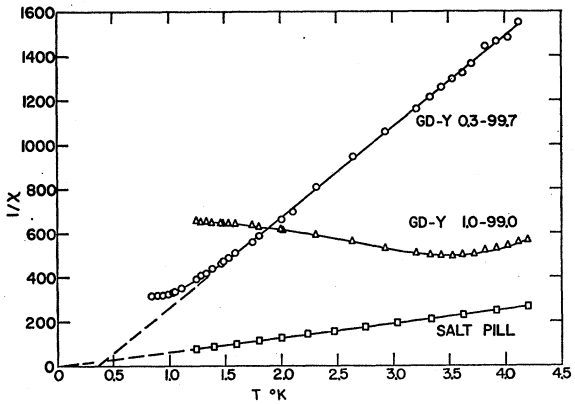

FIG. 2. Inverse susceptibility vs temperature for 1.0 at. % Gd and 0.3 at. % Gd alloys. Calibration data for an iron alum salt pill are also shown.

[4] P. M. Hall, S. Legvold, and F. H. Spedding, Phys. Rev. **116**, 1446 (1959).

[5] See, for example, D. deKlerk, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 74.

[6] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Research Natl. Bur. Standards **64A**, 1 (1960).

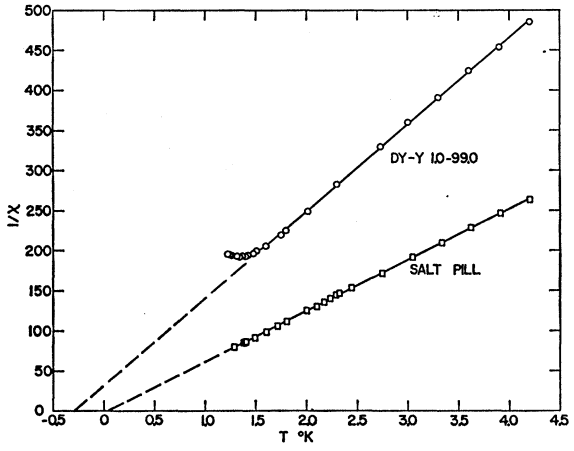

FIG. 3. Inverse susceptibility vs temperature for a 1.0 at. % Dy alloy. Calibration data for an iron alum salt pill are also shown.

and the bath was maintained by helium exchange gas in the sample chamber at a pressure of about 1 mm Hg.

Adiabatic demagnetizations were performed on all samples from initial conditions approximating 1.2°K and 11 koe. In each case, the temperature after demagnetization was determined from resistance measurements of a calibrated carbon resistor.

RESULTS

Susceptibility Measurements

The data obtained from susceptibility measurements are presented in the graphs of Figs. 2–4 with inverse susceptibility $1/\chi$ plotted vs T. Calibration data with a pill of iron ammonium alum are given in each case. Minima in $1/\chi$ are observed at 3.4°K for the 1.0 at. % Gd alloy, and at 1.3°K for the 1.0 at. % Dy alloy. There is an apparent approach to a minimum in $1/\chi$ near 0.8°K for the 0.3 at. % Gd alloy. There is no evidence for a minimum in $1/\chi$ for the Ho alloys.

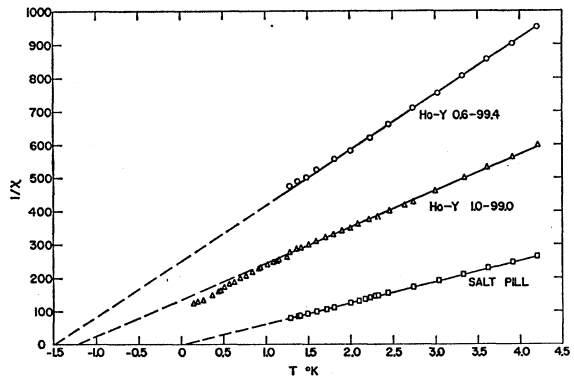

FIG. 4. Inverse susceptibility vs temperature for 0.6 at. % Ho and 1.0 at. % Ho alloys. Calibration data for an iron alum salt pill are also shown.

TABLE II. Adiabatic demagnetization data.

Sample	Initial field (koe)	Initial temperature (°K)	Temperature after demagnetization (°K)
0.3% Gd[a]	10.0	1.25	0.80
0.6% Ho[a]	11.4	1.29	1.04
1.0% Ho[a]	11.4	1.28	0.91
0.6% Ho[b]	12.0	1.25	0.83
1.0% Ho[b]	11.4	1.25	0.76

[a] Polycrystalline sample.
[b] Single crystal with a axis parallel to the magnetic field.

Magnetization Measurements

The results of the magnetization measurements along the a and c directions of the 0.6 at. % Ho alloy are shown in the graph of Fig. 5 and for the 1.0 at. % Ho alloy in the graph of Fig. 6. The magnetization σ in emu/g is plotted vs magnetic-field strength H in koe for various temperatures T. The ratio of the magnetization along the a axis to that along the c axis at 11 koe and 4.2°K is about 4 for the 0.6 at. % Ho alloy and about 5 for the 1.0 at. % Ho alloy. Saturation magnetizations were obtained by extrapolation of the σ vs $1/H$ plots. The saturation magnetizations obtained in this way are 2.9 emu/g for the 0.6 at. % Ho alloy and 4.8 emu/g for the 1.0 at. % Ho alloy. Using these extrapolated values of saturation moments, magnetizations were computed from the Brillouin formula at 1.47°K for the 0.6 at. % Ho alloy and at 1.49°K for the 1.0 at. % Ho alloy. These calculated data are represented by the dashed curves of Figs. 5 and 6. It can be seen that the experimental points fall considerably below these calculated curves for both alloys.

Hysteresis was observed in the 1.0 at. % Ho alloy at 1.58°K with the a axis parallel to the field by measuring σ with the magnetic field first increasing and then decreasing. The data are presented in the graph of Fig. 7 with σ in emu/g plotted vs H in koe. This aspect

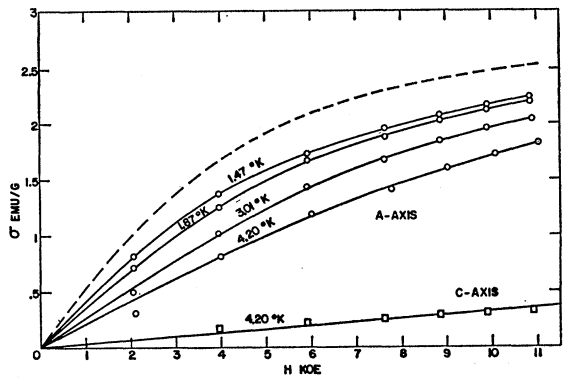

FIG. 5. Magnetization σ in emu/g vs magnetic-field strength H in koe for the 0.6 at. % Ho single crystal. The lowest curve is for H parallel to the c axis, whereas the upper curves are for H parallel to the a axis. The dashed curve represents the expected behavior of an ideal paramagnetic material of saturation moment 2.9 emu/g at 1.47°K.

TABLE III. Comparison of observed and calculated Curie constants for the alloys investigated.

Alloy	C (obs)	C (calc)
0.3 at. % Gd	0.0023	0.0012
1.0 at. % Dy	0.0076	0.0071
0.6 at. % Ho	0.0056	0.0043
1.0 at. % Ho	0.0085	0.0071

was not investigated for the 0.6 at. % Ho alloy or in the other crystalline directions.

Adiabatic Demagnetization Measurements

Adiabatic demagnetizations were performed on those samples which did not show a minimum in the plot of inverse susceptibility vs temperature. The starting temperature, initial field, and temperature after demagnetization are listed in Table II for those materials investigated. Demagnetizations were performed on the single crystals with the a axis parallel to the magnetizing field.

DISCUSSION

A comparison of the observed Curie constants and those computed on the basis of ideal paramagnetic behavior is shown in Table III. It is apparent that the observed Curie constants are somewhat larger than expected on the basis of the calculations. Only a small part of the difference can be explained by the presence of impurities in the samples. From the hysteresis measurements on the 1.0 at. % Ho single crystal it is apparent that there is a certain small amount of ferromagnetism in this alloy. If this is due to ferromagnetic clustering of the solute metal, one would expect this to be present to some extent in all the alloys, representing a small departure from random dispersal of the solute atoms. This, in turn, would enhance the susceptibility and help account for the larger observed values. It should also be mentioned that Sato *et al.*[7] have pointed out that the $1/\chi$ vs T curves for dilute alloys exhibit a slope which increases with temperature. Thus, the Curie constant obtained from the slope of the curve would be overestimated at all but the high temperatures (near room temperature).

Magnetic transitions characteristic of antiferromagnetism were observed at 3.40°K in the 1.0 at. % Gd alloy and at 1.34°K for the 1.0 at. % Dy alloy. Néel[8] has suggested that the magnetic transition temperature be determined by a spin-spin interaction. DeGennes[9] has suggested that the spin-spin interaction be modified to include the effects of spin-orbit coupling. The lower Néel temperature obtained for the 1.0 at. % Dy alloy as

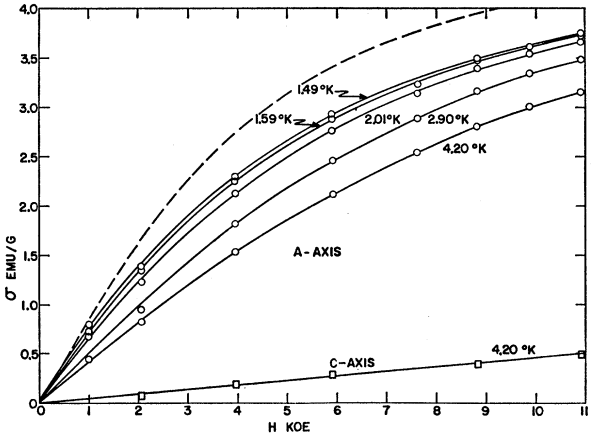

FIG. 6. Magnetization σ in emu/g vs magnetic-field strength H in koe for the 1.0 at. % Ho single crystal. The lowest curve is for H parallel to the c axis, whereas the upper curves are for H parallel to the a axis. The dashed curve represents the expected behavior of an ideal paramagnetic material of saturation moment 4.8 emu/g at 1.49°K.

compared to the 1.0 at. % Gd alloy is in fair agreement with either of these proposals. There is evidence of an approaching transition at 0.8°K in the 0.3 at. % Gd alloy. Thoburn *et al.*[10] have determined the paramagnetic Curie temperatures and Néel points of gadolinium-yttrium alloys with large gadolinium concentrations. An extrapolation of their data to small gadolinium concentrations gives expected transition temperatures of

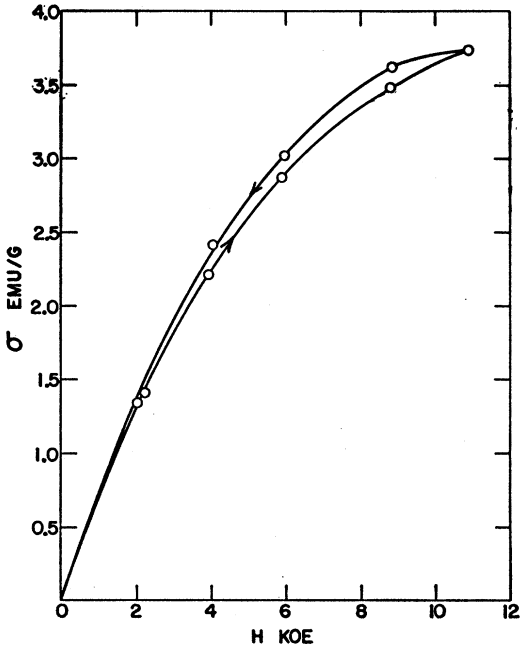

FIG. 7. σ versus H at 1.58°K for the 1.0 at. % Ho single crystal with field increasing and decreasing and with the a axis parallel to the field.

[7] H. Sato, A. Arrott, and R. Kikuchi, J. Phys. Chem. Solids **10**, 19 (1959).
[8] L. Néel, Compt. rend. **206**, 49 (1938).
[9] P. G. deGennes, Compt. rend. **247**, 1836 (1958).
[10] W. C. Thoburn, S. Legvold, and F. H. Spedding, Phys. Rev. **110**, 1298 (1958).

4°K and 1°K for the 1.0 at. % and 0.3 at. % alloys, respectively. These numbers are in reasonable agreement with the present results.

The amount of cooling obtained by adiabatic demagnetization of the various samples was small. It was somewhat greater for the single crystals along the easy direction of magnetization than for the polycrystalline samples of the same alloys. In an effort to understand why such small temperature reductions were obtained, calculations have been made of certain entropy changes involved in the demagnetization process for the two single-crystal samples. The actual entropy $(\Delta S/R)_{\text{actual}}$ removed per mole during isothermal magnetization has been computed from the magnetization curves of Figs. 5 and 6. The Brillouin formula has been used to calculate the entropy change $(\Delta S/R)_{\text{ideal}}$ during magnetization, treating the alloy as an ideal paramagnetic material. Finally, the change in entropy $(\Delta S/R)_{\text{el}}$ of the conduction electrons between the initial and final temperatures of demagnetization has been calculated using the electronic entropy for pure yttrium. Jennings *et al.*[11] have reported that the electronic entropy of yttrium is $85\times10^{-4}T$ joules/mole °K and that the lattice entropy is negligible in comparison near 1°K. The calculated quantities are presented in Table IV as they apply to the 0.6 at. % Ho and 1.0 at. % Ho single crystals. It is to be noted that $(\Delta S/R)_{\text{ideal}}$ is about 6 times the value of $(\Delta S/R)_{\text{actual}}$ for both alloys. This indicates that the behavior of the alloys is far from ideal at the temperature of magnetization. The entropy change of the conduction electrons is considerably less than the actual entropy change between the initial and final temperatures. There is, thus, a rather large contribution to the heat capacity, probably from the magnetic spins, at temperatures in the range 0.7–1.2°K for these alloys. The mechanism responsible for this anomalous behavior and consequent feeble cooling during demagnetization is not understood. It is apparent that the behavior of the alloys at these temperatures is such as to render them unsuitable for magnetic cooling purposes.

TABLE IV. Entropy changes encountered in magnetization and demagnetization of the 0.6 at. % Ho and 1.0 at. % Ho single crystals.

Sample	$(\Delta S/R)_{\text{ideal}}$	$(\Delta S/R)_{\text{actual}}$	$(\Delta S/R)_{\text{el}}$
0.6 at. % Ho	0.009	0.0016	0.0004
1.0 at. % Ho	0.015	0.0020	0.0005

ACKNOWLEDGMENTS

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[11] L. D. Jennings, R. Miller, and F. H. Spedding, J. Chem. Phys. (to be published).