CONF-901029--1

DE91 001520

PERFORMANCE COMPARISON OF MAGNETIC REFRIGERATION CYCLES

F. C. Chen, G. L. Chen, R. W. Murphy, and V. C. Mei
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

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.

To Be Presented at the
Cryocooler - 6
Plymouth, Massachusetts
October 25-26, 1990

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

---

*Research sponsored by the Office of Industrial Technologies, U.S. Department of Energy, operated by Martin Marietta Energy Systems, Inc. under Contract No. DE-AC05-84OR21400.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PERFORMANCE COMPARISON OF MAGNETIC REFRIGERATION CYCLES

F. C. Chen, G. L. Chen, R. W. Murphy, and V. C. Mei
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

ABSTRACT

Magnetic refrigeration has been used for cryogenic cooling at temperatures near absolute zero for many years. In these cases, a single-step adiabatic demagnetization method that does not provide continuous refrigeration is commonly used. The possibilities of providing continuous cooling through magnetic refrigeration cycles and of extending the range of applications above near-absolute-zero temperatures have been investigated only in recent years. This paper reports the results of a parametric performance study of three magnetic refrigeration cycles using four rare-earth magnetic materials operating near their respective Curie temperatures. The thermodynamic cycles employed are the magnetic-equivalent Carnot, Ericsson, and ideal regenerative cycles, and the four magnetic materials are terbium, holmium, erbium, and thulium. Our findings show that the Carnot cycle is not possible for cases of temperature lift beyond 10 K for a magnetic field variation of 7 Tesla, that the performance and capacity of an ideal regenerative cycle are higher than that of the corresponding Ericsson cycle, and that the magnetocaloric effects of erbium and thulium seem to be too weak for practical applications.

INTRODUCTION

The concept of magnetic refrigeration can be traced back to more than half a century when researchers needed to produce cooling at near-absolute-zero temperature. In 1933 Giauque achieved a cooling from 3.5 K down to 0.5 K by utilizing the magnetocaloric effect of solid materials.[1] His method was to cool a paramagnetic salt to 3.5 K in a magnetic field and then to adiabatically demagnetize it to achieve 0.5 K. This adiabatic demagnetization method is a one-shot or single-step cooling process that cannot provide continuous refrigeration.

The possibility of constructing a magnetic refrigerator using the magnetocaloric effect to produce continuous refrigeration was suggested by Daunt in 1949.[2] He combined two isothermal and two adiabatic magnetization and demagnetization processes to form a magnetic Carnot cycle capable of providing sustained refrigeration. The laboratory experimentation on this concept was not performed until the mid '70s, when Brown built and tested a reciprocating magnetic refrigerator assembly using gadolinium at the working medium[3], and Barclay experimented with a rotary wheel concept using continuous magnetic refrigeration to make liquid helium.[4]

In ultra-low-temperature applications, a temperature lift of a few degrees in a cryogenic environment is often sufficient and can be easily achieved by a simple magnetic refrigeration cycle using relatively low magnetic field changes. To extend magnetic refrigeration to other temperature ranges and other types of applications in which the temperature lift is more than just a few degrees requires a high magnetic field, more involved cycle processes, or materials having a large magnetocaloric effect.

Recent discoveries of new high-temperature superconducting materials that can provide higher magnetic fields than previously achievable has prompted renewed interest in magnetic refrigeration for wider ranges of applications. Until newer materials with larger magnetocaloric effects are found, more complicated thermomagnetic cycle processes are necessary to achieve refrigeration over large temperature spans. This paper examines the characteristics of three thermomagnetic refrigeration cycles, viz., Carnot, Ericsson, and ideal regenerative cycles using four rare-earth materials as working media operating near their respective Curie temperatures.

MAGNETOCALORIC EFFECT OF WORKING MEDIA

The four rare-earth materials chosen as the working media for this study are terbium (Tb), holmium (Ho), erbium (Er), and thulium (Tm). The Curie temperatures of this group vary from 230 K to 56 K. Because these are pure metals, their thermomagnetic properties may be approximated by simplified theories.

Magnetic refrigeration is created by the entropy change of a magnetic material subjected to changes in external magnetic field and temperature. The solid working media consist of many particles that interact by means of lattice vibrations, ions spins, and conduction electron flow. When a working solid is exposed to a change in external magnetic field or in temperature, the entropy changes accordingly. The magnetic-field-induced adiabatic temperature change and the heat capacity are two key parameters for determining the usefulness of a magnetic working medium. All three above-mentioned interactions affect the change in heat capacity and adiabatic temperature. Among them, the conduction electron flow effect is the weakest, and the lattice vibration contribution is often negligible at ultra-low temperatures. However, at normal cryogenic temperatures, all three effects have to be taken into account.

In thermomagnetic cycle analysis, the magnetocaloric effect of a working medium is often expressed in terms of the temperature-entropy-magnetic field (T-S-H) relationship. This relationship can be determined by the molecular mean-field theory (MFT) or by experiments. The MFT has been used to compute the thermomagnetic properties of gadolinium, and the agreement between computed and experimental results was reasonably good.[5] The simplified MFT is not applicable here because the working medium in this study is either anisotropic, has multiple magnetic phase transitions, or has field-dependent phase transition temperature.

A modified mean-field theory that takes into account the field-dependent nature of the magnetic phase transition temperature (Neel temperature) was developed to compute the thermomagnetic properties of Tb.[6] A comparison between the computed adiabatic temperature changes at 7 Tesla and the experimental data[7] is shown in Fig. 1. A T-S-H plot for Tb derived from the modified MFT using zero-field heat capacity data[8] is shown in Fig. 2.

For magnetic materials (Ho, Er, and Tm) with thermomagnetic behaviors that cannot be predicted by simplified theories, T-S-H relationships were derived from experimentally measured heat capacity at zero field[9-11] and adiabatic temperature changes at applied fields.[12-13] The T-S diagrams of the three working media are shown in Figures 3—5.

THERMOMAGNETIC CYCLES

Three idealized thermodynamic cycles, all having isothermal refrigeration and heat rejection processes, are employed for examining the refrigeration performance and capacity of these working media. They are (1) a Carnot cycle, (2) an Ericsson cycle, and (3) a regenerative cycle. These cycle envelopes on a representative T-S-H diagram are shown in Fig. 6.

For a given magnetic field variation, i.e., the low and the high field in which a cycle will be operating, a magnetic Carnot cycle will have two isothermal heat transfer processes and two isentropic processes that form a rectangle between these two low and high field curves on the T-S diagram. Because the Carnot cycle rectangle must fit between the two field operating curves, the maximum temperature lift the Carnot cycle can achieve is limited, and temperature lifts beyond that are not achievable by magnetic Carnot cycle.

A magnetic Ericsson cycle comprises two isothermal heat transfer processes and, ordinarily, two constant-field processes in which the heat rejected in one of the constant-field processes is recovered in the other constant-field process. This cycle is often referred to as the constant-field cycle because two constant-field processes are involved. Because the magnetic field curves are not parallel to each other, the

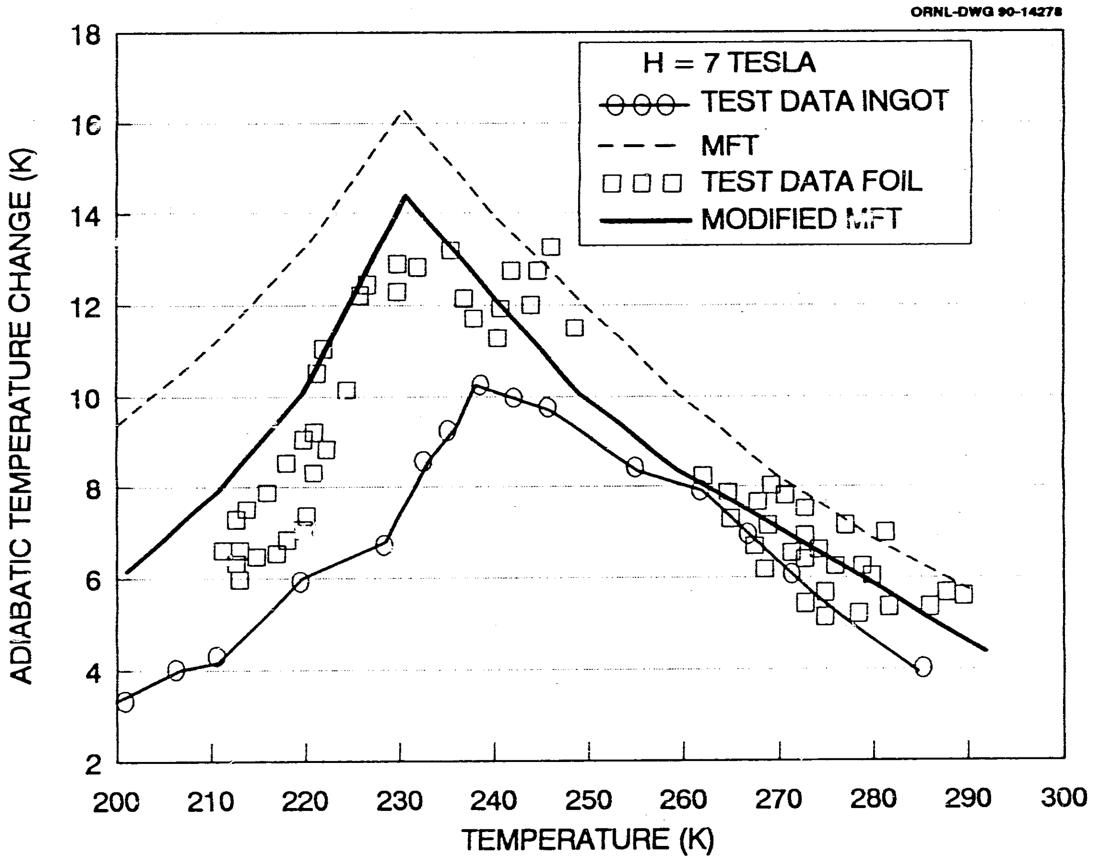

Fig. 1. Change in temp. vs. initial temp. for terbium and Green data

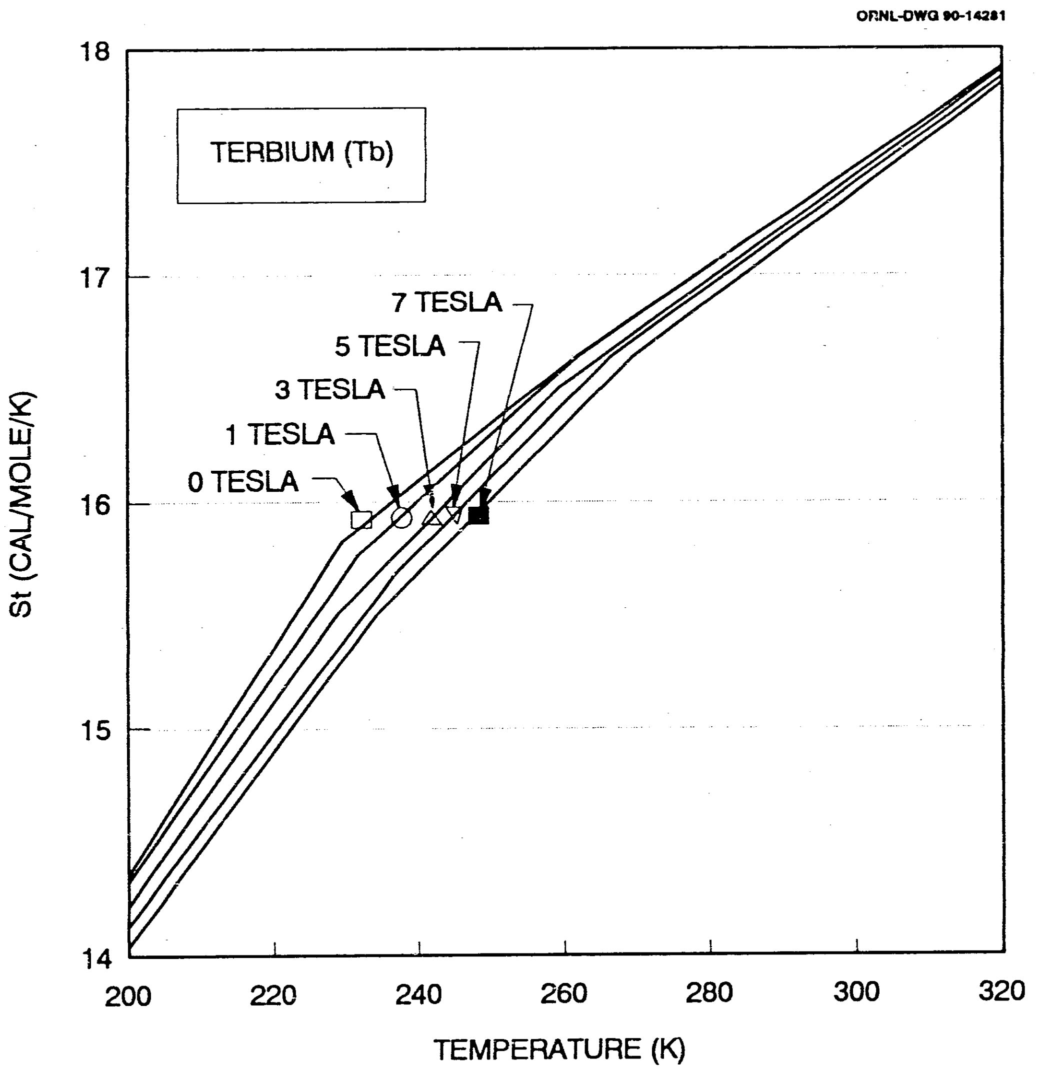

Fig. 2. Total entropy of Tb as a function of temp. and magnetic field

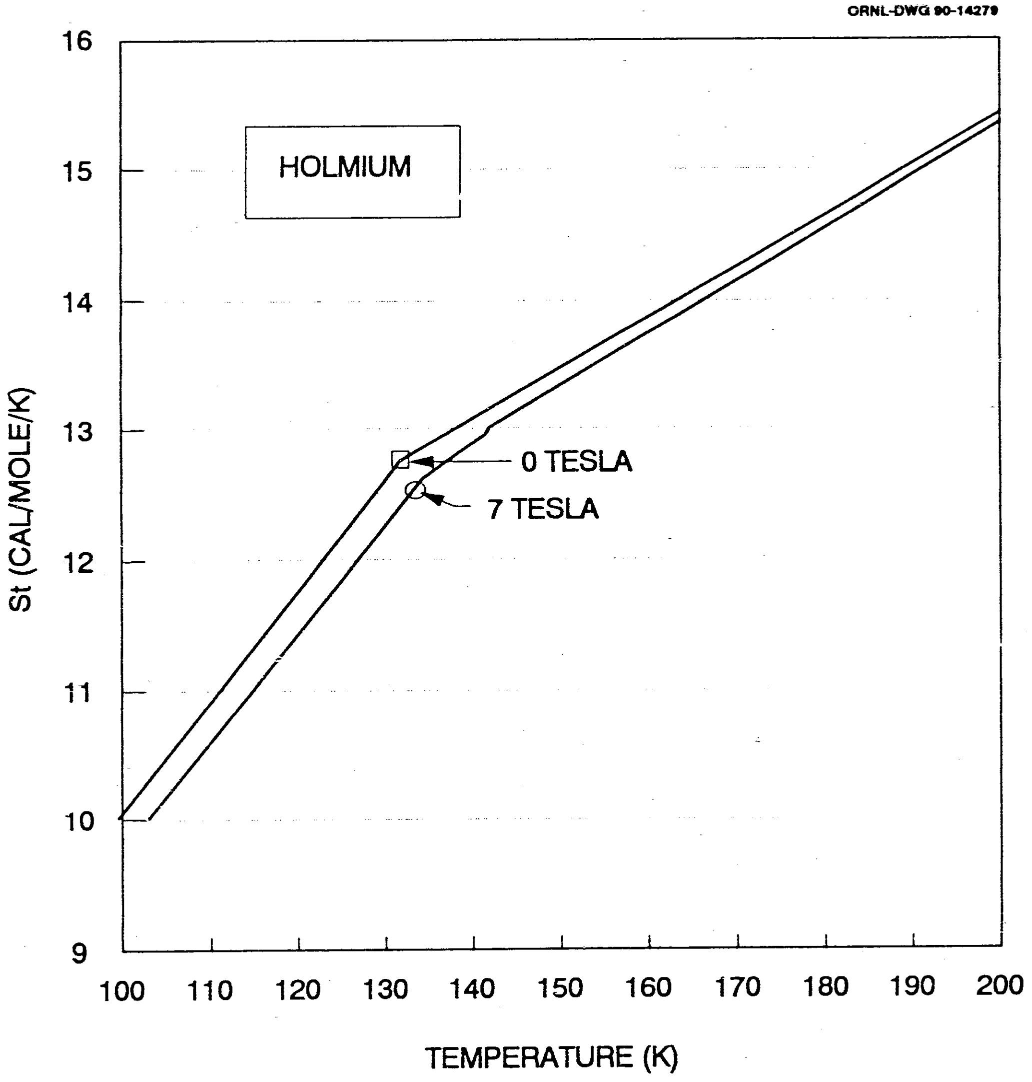

Fig. 3. Total entropy of Ho as a function of temp. and H

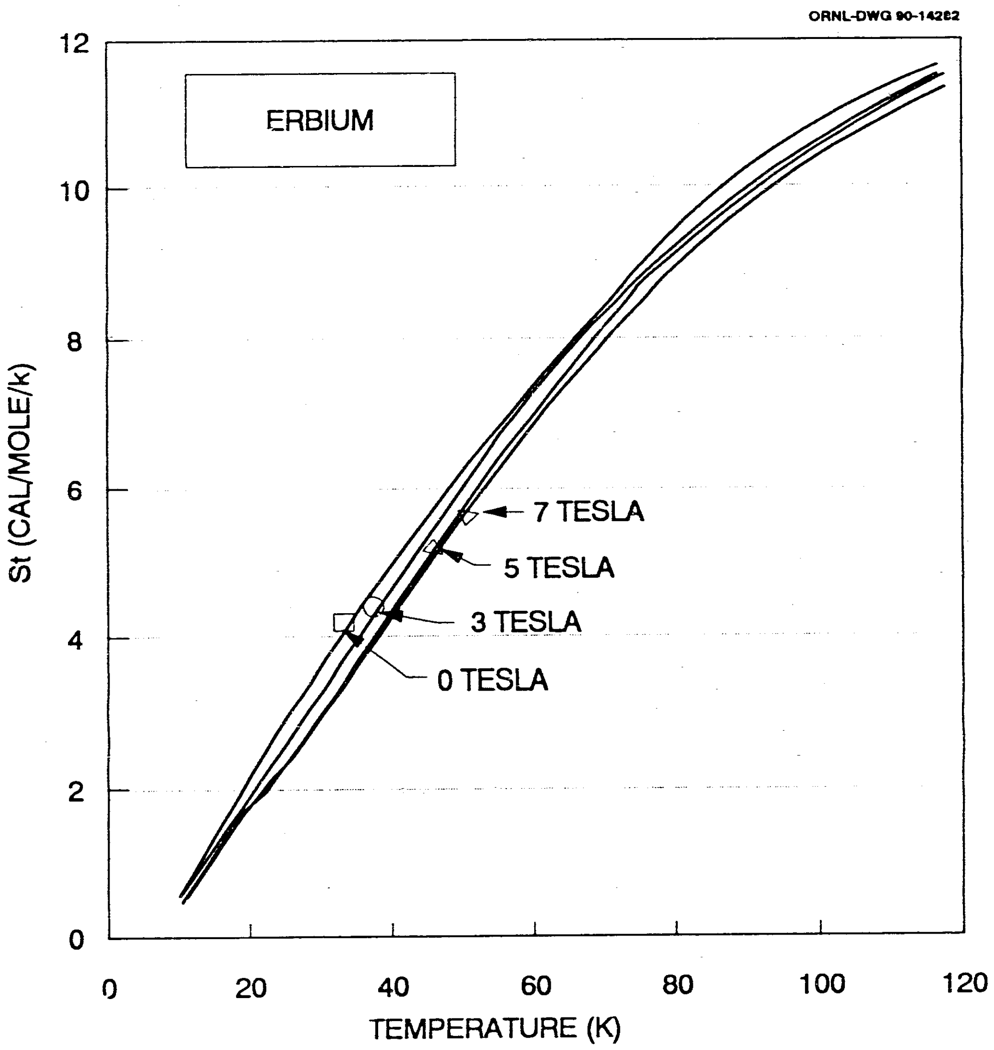

Fig. 4. Total entropy of Er as a function of temp. and H

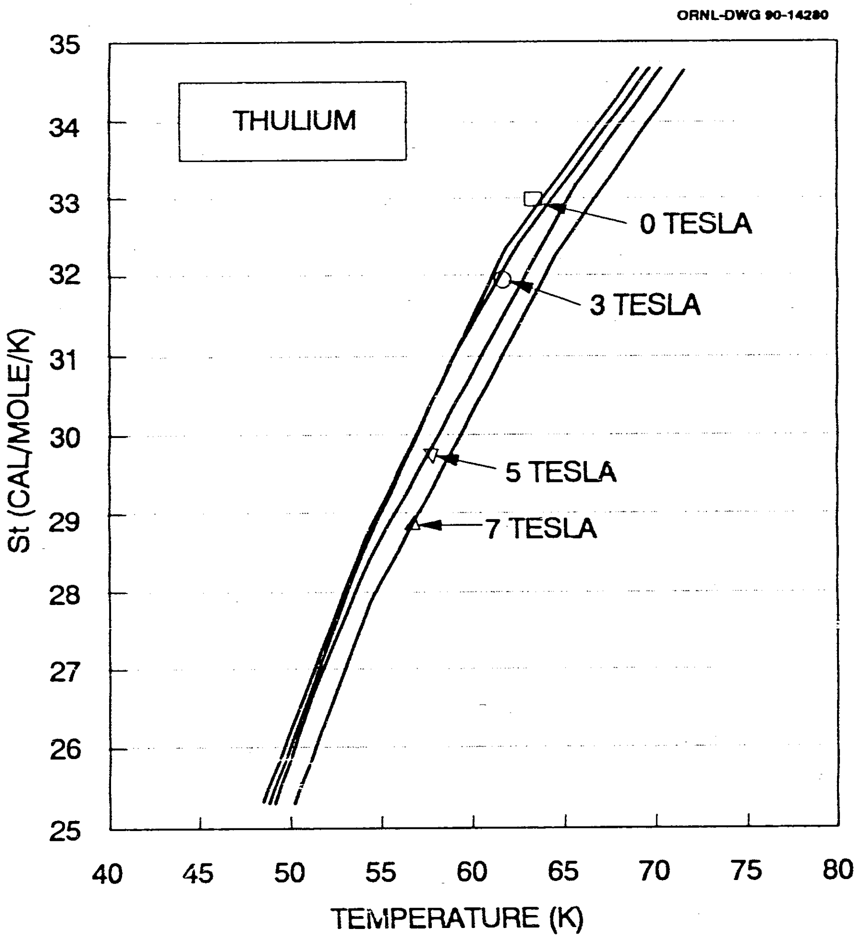

Fig. 5. Total entropy of Tm as a function of temp. and H

ORNL-DWG 90-14284

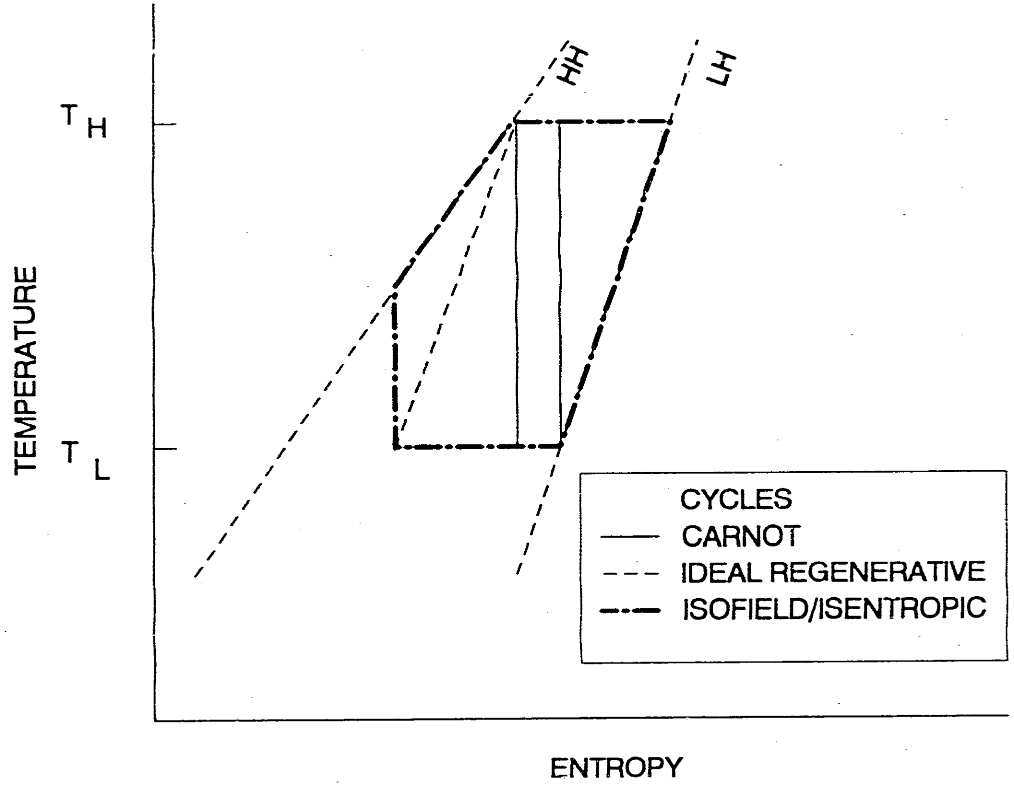

Fig. 6. T-s with constant field lines for Carnot, ideal regenerative, and constant-field cycles.

internal energy balance between the low and the high constant-field processes can not be maintained. To maintain the energy balance, either excess heat must be rejected to the ambient or part of the constant-field process must be terminated and substituted for by adiabatic process,[14] as shown in Fig. 6, resulting in cycle irreversibilities. The magnetic Ericsson cycle can achieve higher temperature lifts than can the Carnot cycle, but it is less energy efficient.

An ideal regenerative cycle consists of two isothermal heat transfer processes, one constant-field process, and one nonisothermal process. The latter process has a varying field path that maintains a fixed horizontal separation parallel to that of the constant-field process on the T-S diagram. Because the two nonisothermal processes of the cycle are parallel, the theoretical regenerative heat transfer between them is internally balanced and there is no theoretical cycle irreversibility loss. Theoretically, this cycle has Carnot efficiency and, in principle, its temperature lift is not limited.

PARAMETRIC ANALYSIS

Using the available T-S-H information for the four working media, the performance and refrigeration capacity of the three magnetic refrigeration cycles are parametrically studied as functions of temperature lift that centers around their respective transition (Curie or Neel) temperatures (Tc = 230 K for Tb, 133 K for Ho, 85 K for Er, and 56 K for Tm). The given magnetic-field limits for the study are 0 and 7 Tesla. The coefficient of performance (COP) and the cooling capacity (Qc) were calculated as a function of cycle temperature range for the four working media. We found that the temperature lift for the Carnot cycle is very limited: it can only span 10 K (centered around the transition temperature) for Tb, 5 K for Ho, 4 K for Er, and 2 K for Tm. The COP and Qc for the constant field and the ideal regenerative cycles are presented in Figures 7—10.

As shown in the figures, an ideal regenerative cycle (IRC) always performs better than the corresponding constant-field cycle (CFC). The differences between them for small temperature lifts near the metal transition point are not very large. In the case for Tb shown in Fig. 7, the cycle performance variation is gradual even at 60 K temperature lift. This is not the case for the other three working media. For these metals, the performance changes are relatively sharp, and the CFC cannot even exist for Tm for a temperature lift beyond 30 K.

PERFORMANCE COMPARISON

In magnetic refrigeration a CFC is easier to implement than an IRC. The operation of an IRC requires the control of a variable magnetic field process, which is rather involved because it needs both temperature versus field information and magnetic transfer and storage provisions. An IRC will have Carnot efficiency.

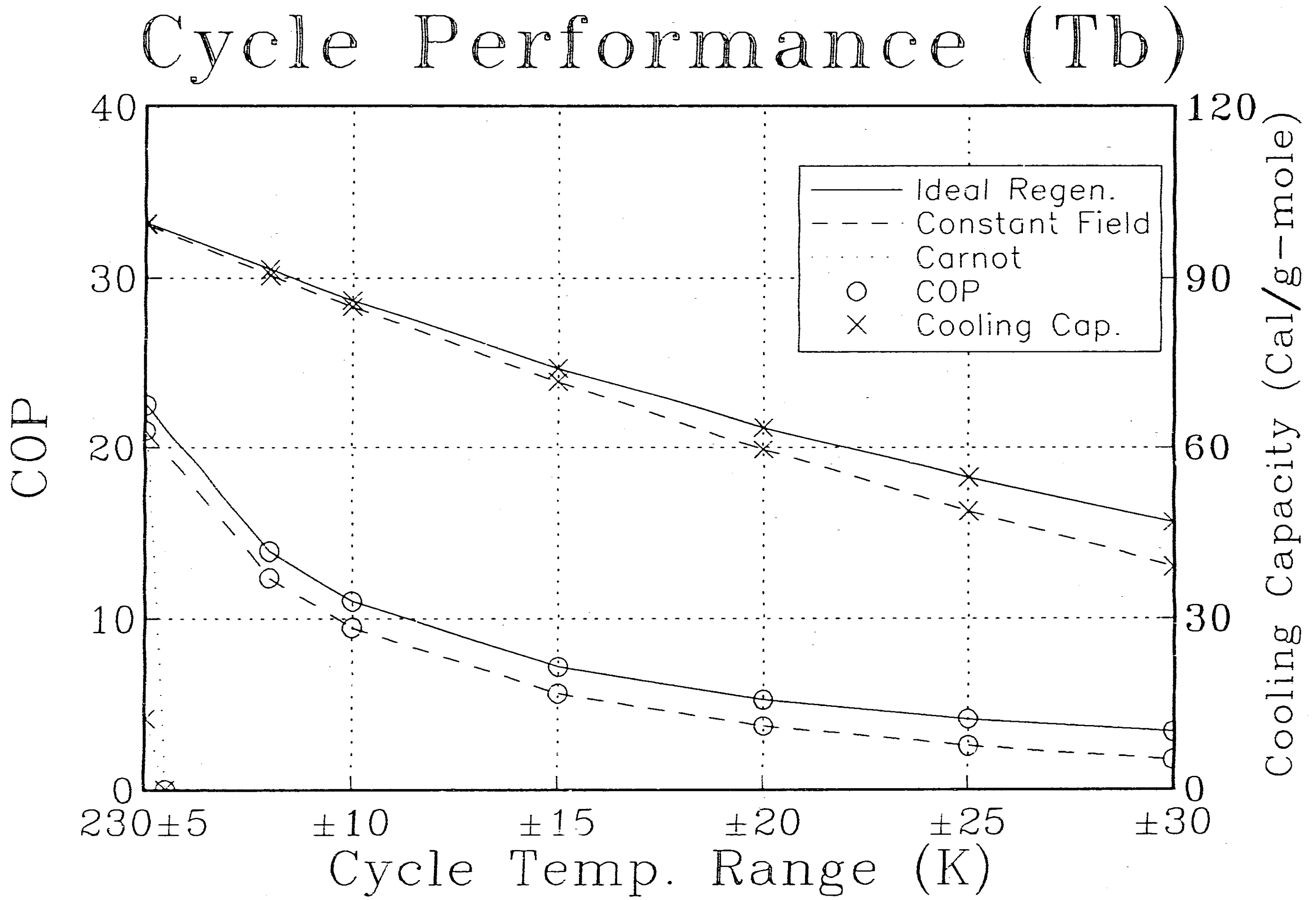

Fig. 7. Cycle performance for Tb

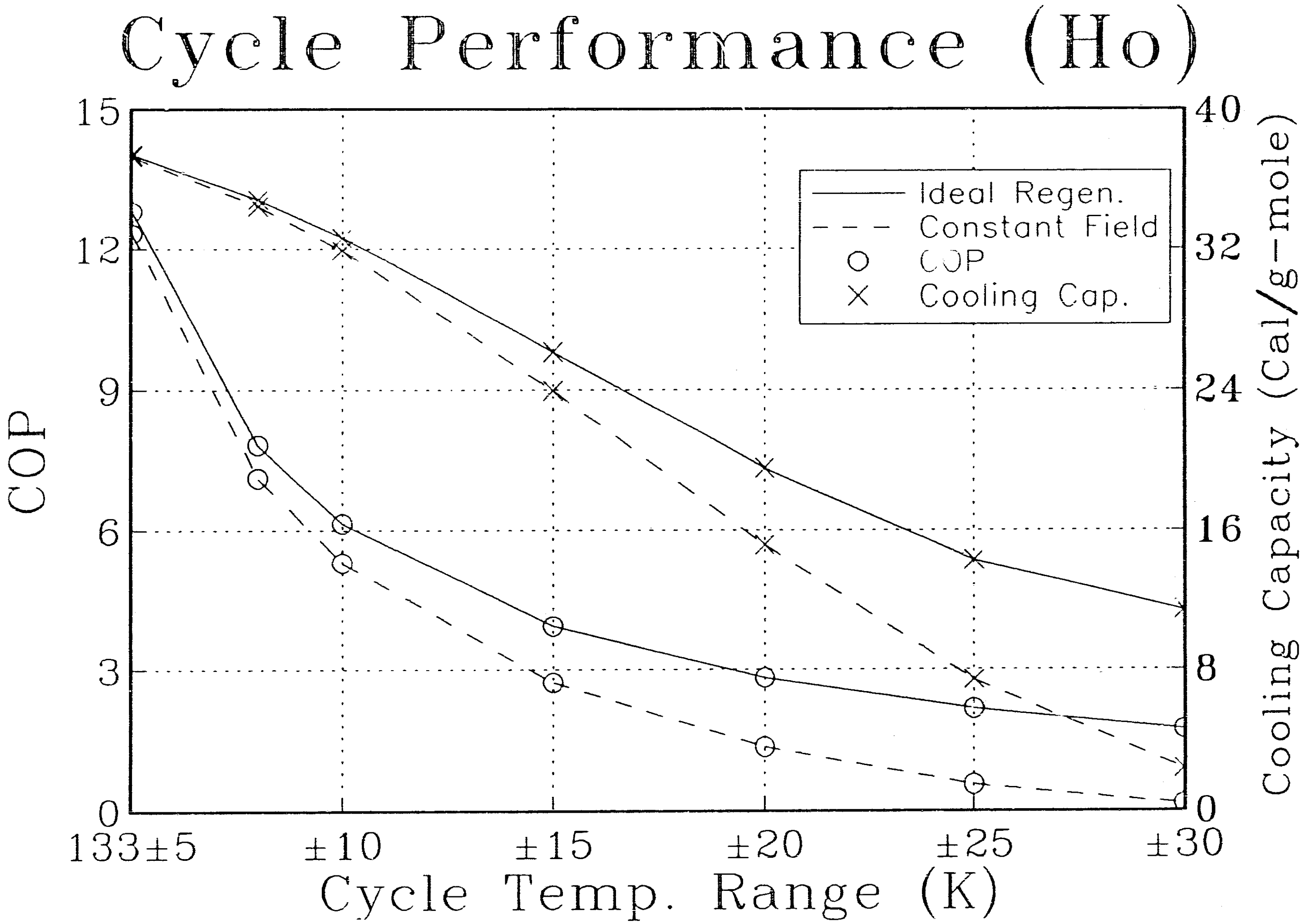

Fig. 8. Cycle performance for Ho

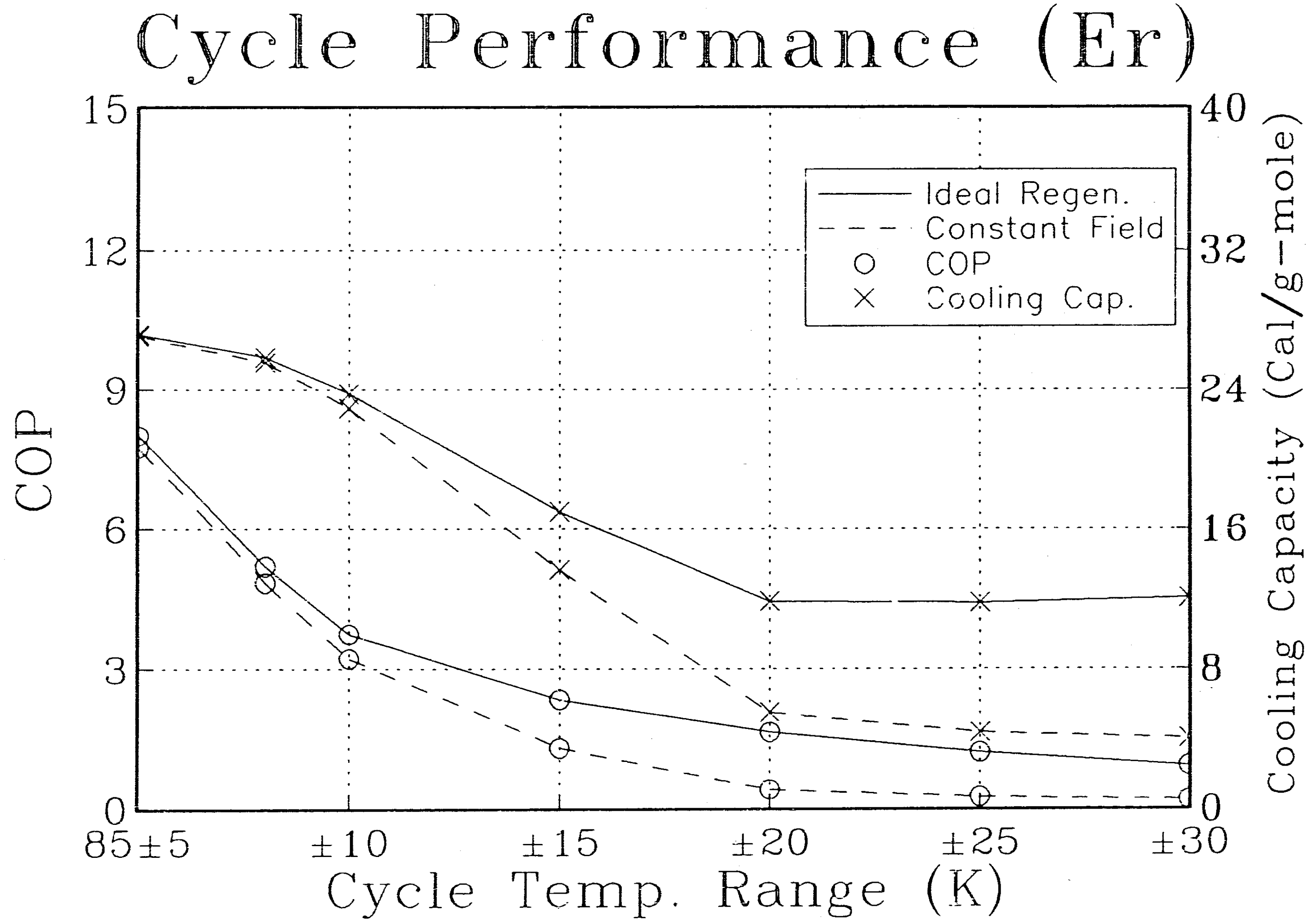

Fig. 9. Cycle performance for Er

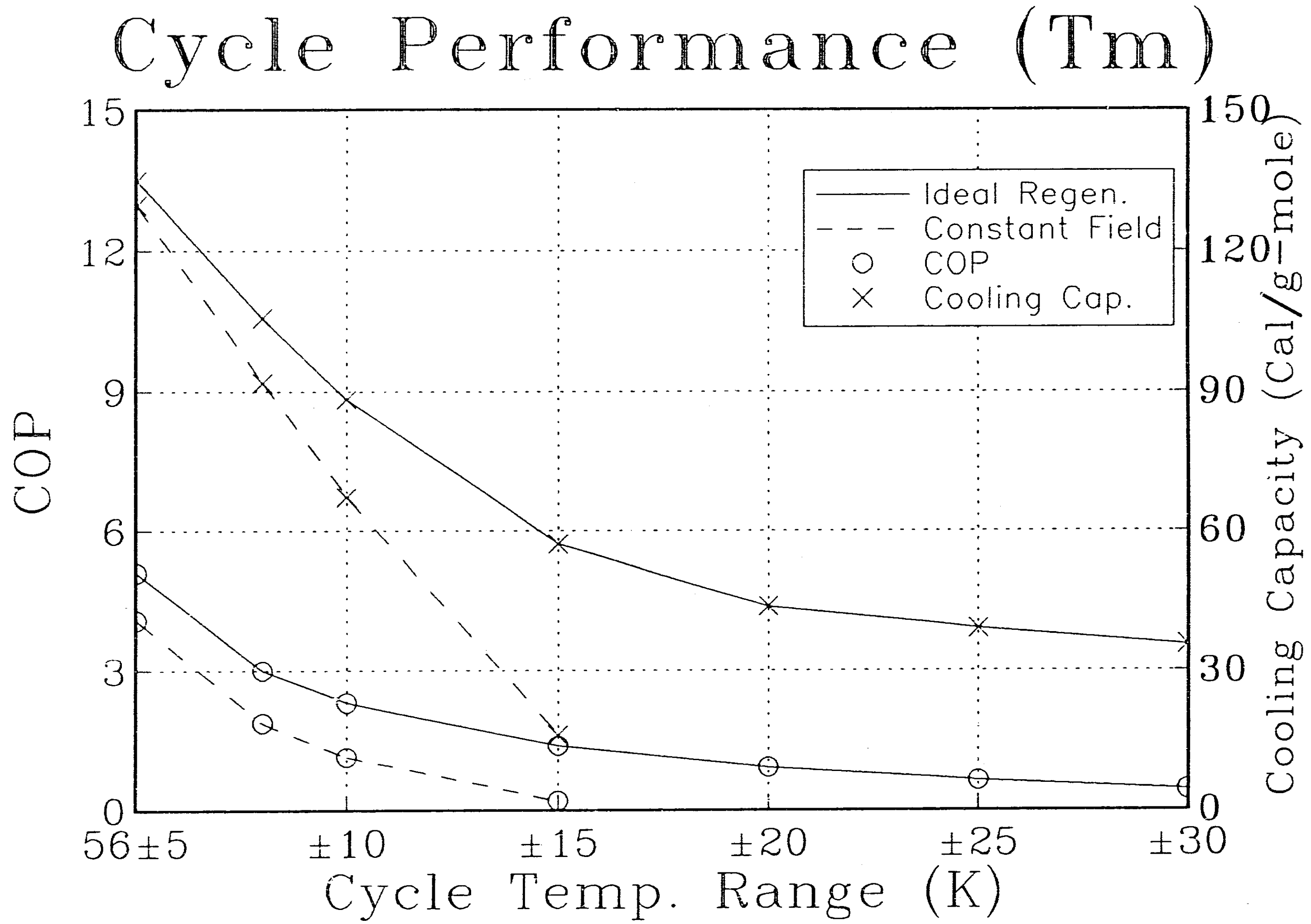

Fig. 10. Cycle performance for Tm

A comparison between the CFC and the IRC would reveal the deviation of the CFC away from the ideal condition. This deviation represents the intrinsic cycle irreversibilities the CFC will have.

The ratios of COP and capacity of the CFC versus IRC as functions of cycle temperature range for Tb are shown in Fig. 11. As can be seen in the figure, the capacity degradation of the CFC is relatively mild. At 60 K temperature lift, the CFC could provide up to 83% of the ideal cooling capacity. But the COP of the CFC degrades faster: it has only about 57% of the ideal COP at 60 K lift.

The performance comparisons of Ho, Er, and Tm are given in Figures 12—14, respectively. For Ho and Er, the degradation of cooling capacity of the CFC is very small for temperature lift up to 20 K. At 20 K lift, the COP degradation is about 8%. Beyond that, both capacity and COP changes will be substantial. In the case of Tm, both the percent cooling capacity and the percent COP of the CFC drop quickly for temperature lift beyond 10 K and reach zero at 34 K lift.

CONCLUDING REMARKS

The performances of three magnetic refrigeration cycles using four rare-earth metals as working media were investigated. The magnetic Carnot cycle has a limited range of application. The IRC has Carnot efficiency and larger-than-Carnot cooling capacity, but requires a nonisothermal variable-field process. The range of applications of the IRC, in principle, is unlimited. The CFC is easier to operate and has been employed in many previous tests and experiments. The inherent CFC irreversible losses are quantified here by comparing them with those of IRC.

Because the IRC has Carnot efficiency, one can analyze the deviation of the CFC from the ideal case by comparing the CFC with the IRC. We observed that the cooling capacity ratio (CR=Qc/Qi) degradation is less than that of the energy efficiency ratio (ER=COPc/COPi) degradation. With Tb as the working medium, we found that CR > 90% for temperature lifts within 50 K (centered around Tc). For the same CR > 90%, the corresponding temperature lift limits for Ho, Er, and Tm are 30 K, 24 K, and 16 K, respectively. Because of the weak thermomagnetic effects of Er and Tm, these two working media may not offer any useful cooling capacity beyond a few degrees of temperature lift. New materials with strong thermomagnetic effects are needed. Performance comparison to analyze cycle irreversible loss using GGG as the working medium is being pursued.

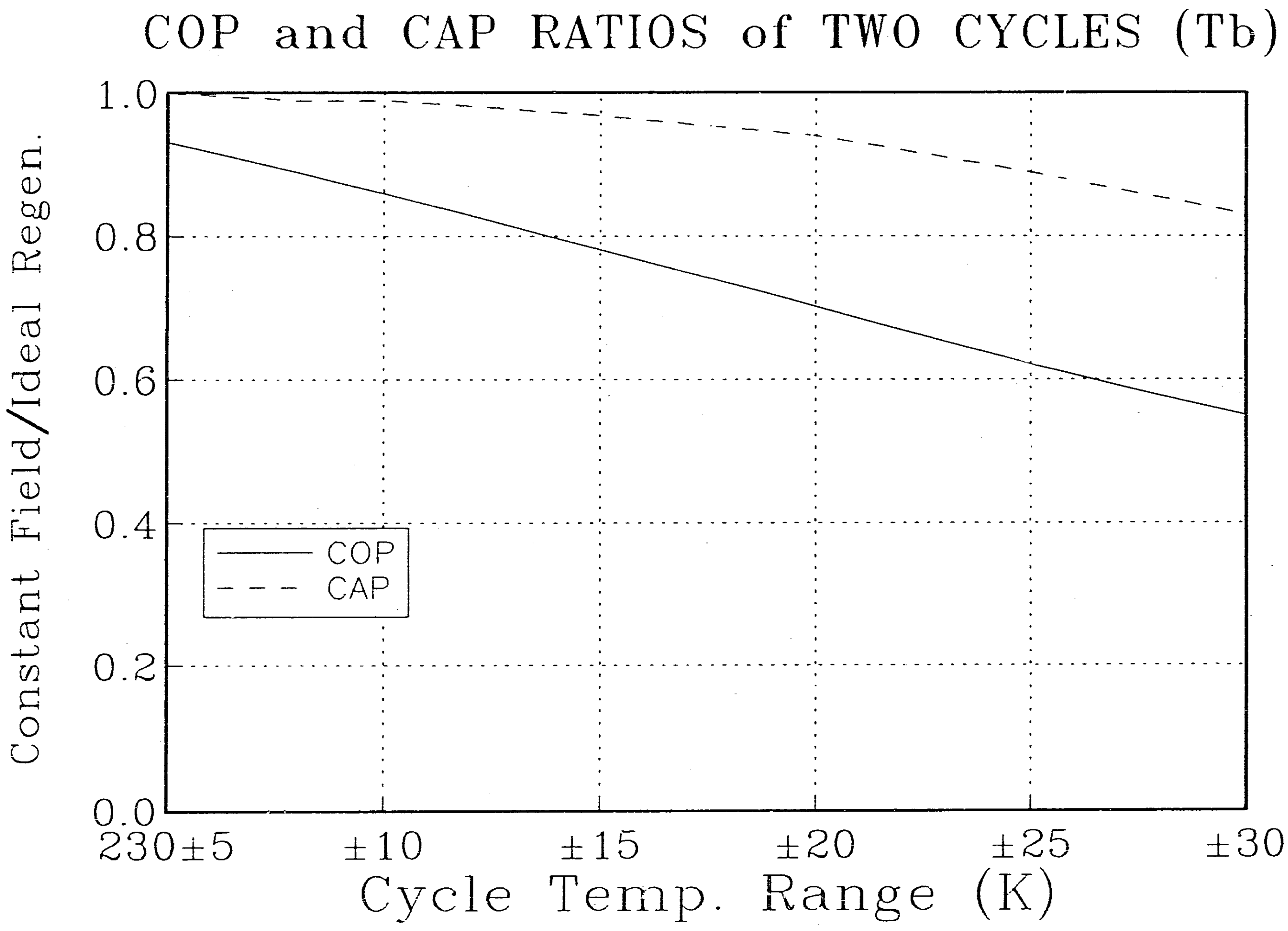

Fig. 11. Cycle performance comparison for Tb

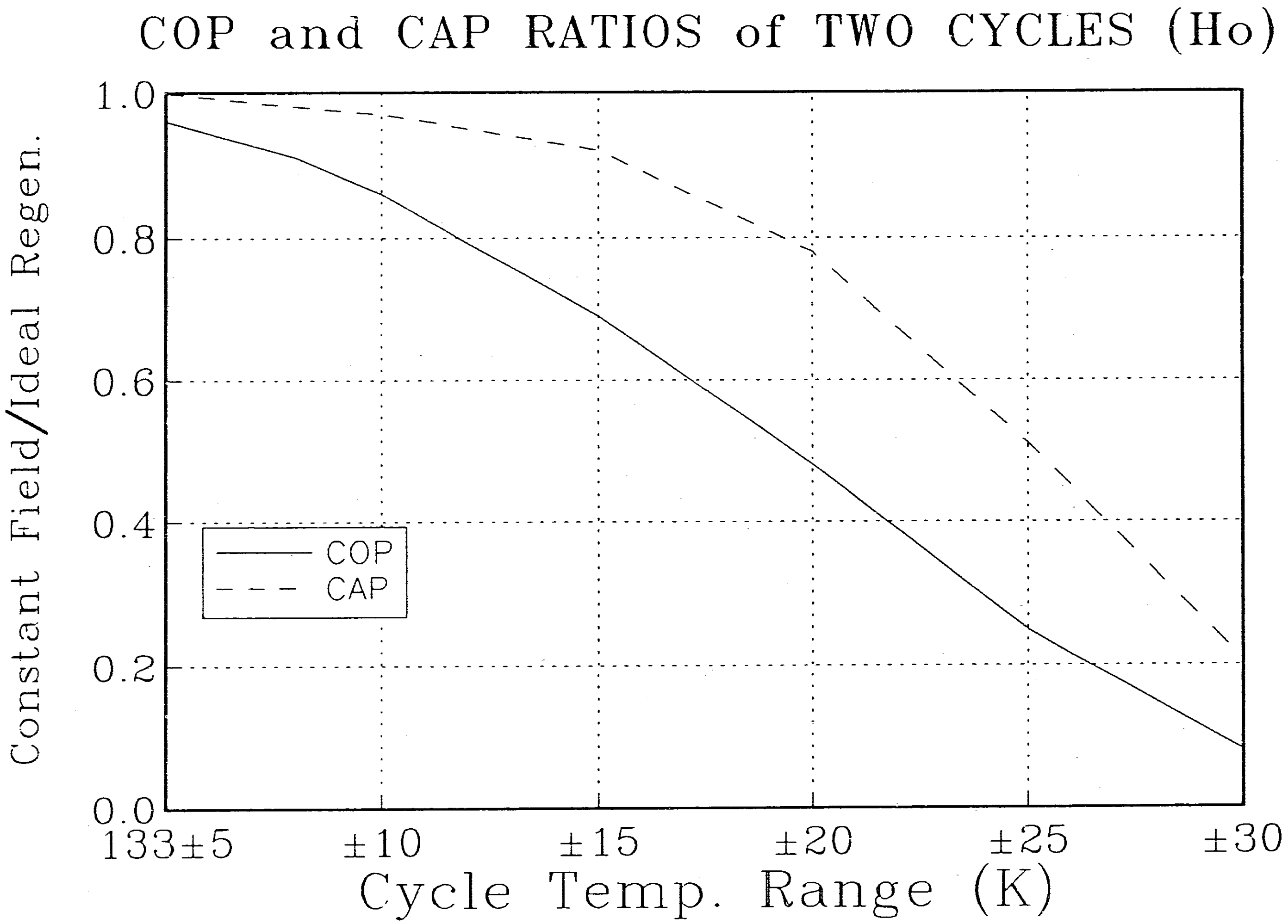

Fig. 12. Cycle performance comparison for Ho

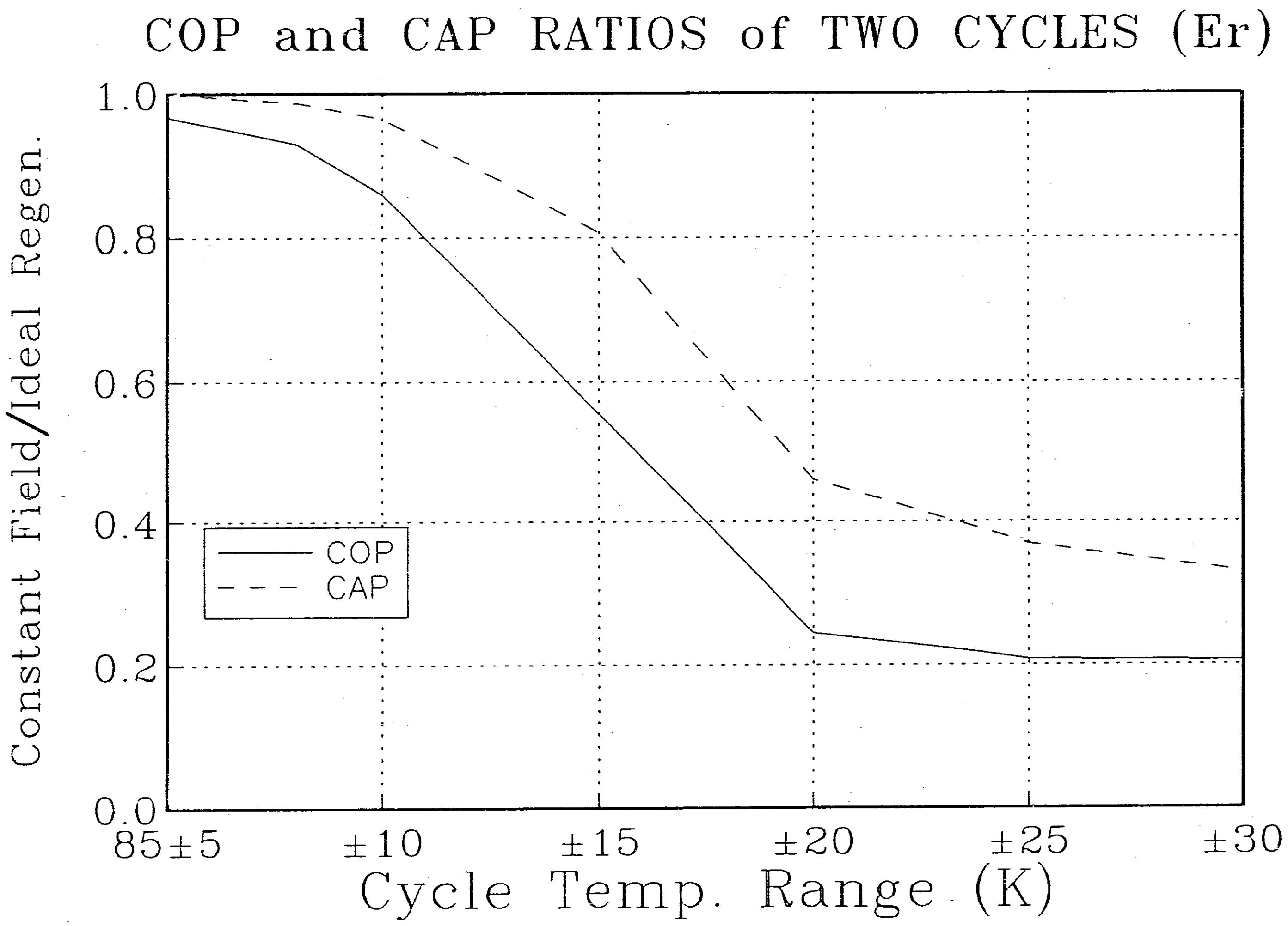

Fig. 13. Cycle performance comparison for Er

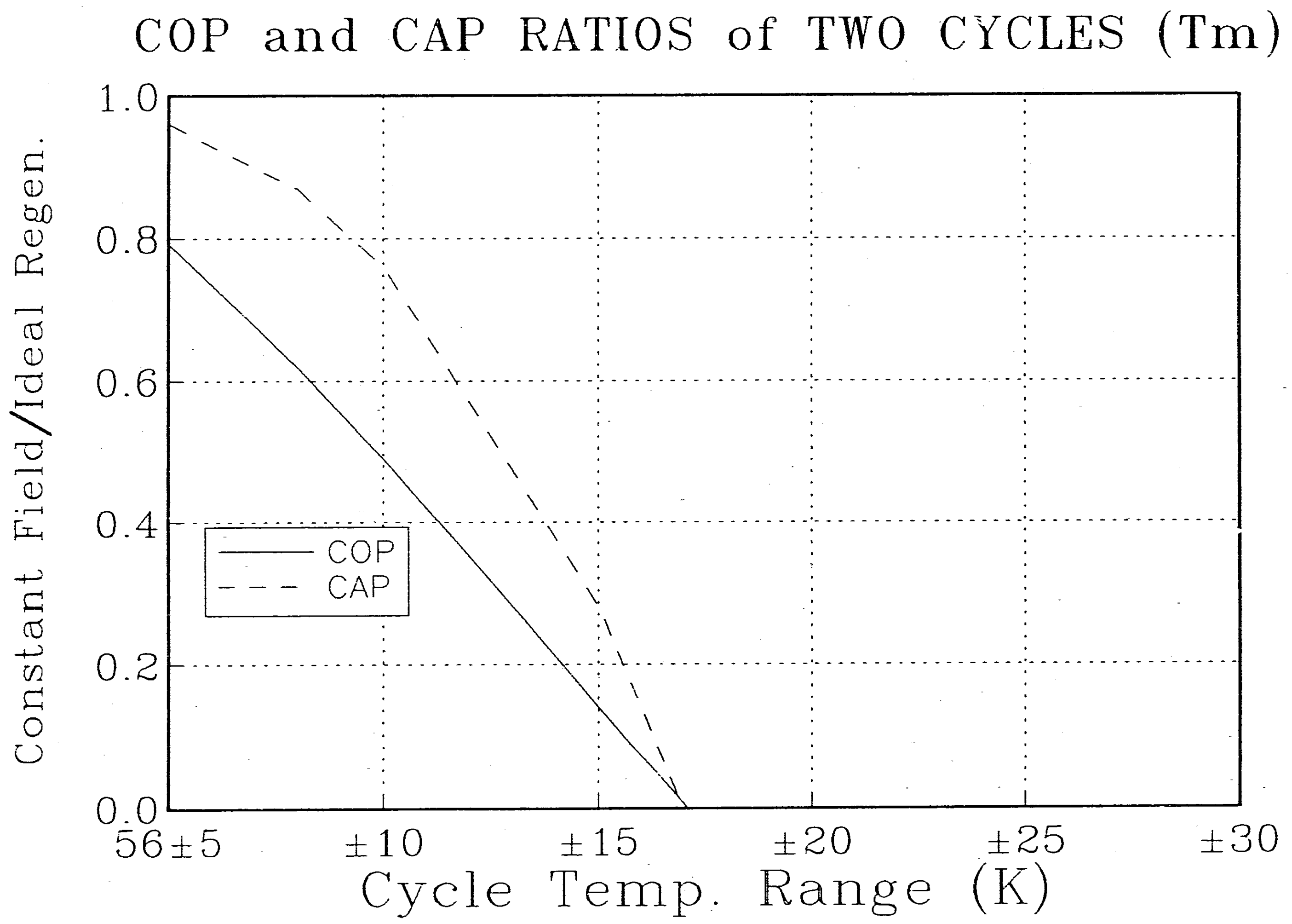

Fig. 14. Cycle performance comparison for Tm

ACKNOWLEDGMENTS

This work was a part of the Thermal Sciences Research Program sponsored by the Advanced Industrial Concepts Division, USDOE, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Authors appreciate the support of M. E. Gunn of DOE during the study; W. R. Levins and J. Holdeman, Jr. for providing review comments; and Pam Gillis and Donna Penland in technical editing services. The initial stage of this work was supported by the Oak Ridge National Laboratory Exploratory Studies Program.

REFERENCES

1. F. Giauque and D. P. MacDougall, "Attainment of Temperatures Below 1 K by Demagnetization of $Gd_2(SO_4)_2 \cdot 8H_2O$," *Phys Rev.*, vol. 43 (1933), p. 768.

2. J. G. Daunt and C. V Heer, "Heat Flow in Metals Below 1 K and a New Method for Magnetic Cooling," *Phys Rev.*, vol. 76 (1949), p. 854.

3. G. V. Brown, J. Appl. "Magnetic Heat Pumping Near Room Temperatures," *Phys* vol. 47, no. 8 (1976), p. 3674.

4. J. A. Barclay and W. A. Steyert, "Magnetic Refrigerator Development," *EPRI Report EL-1757*, (1981).

5. F. C. Chen, R. W. Murphy, et al., "Loss Analysis of the Thermodynamic Cycle of Magnetic Heat Pumps, Phase I Final Report," ORNL/TM-11608, Oak Ridge National Laboratory, in press.

6. D. E. Hegland, S. Legvold, and F. H. Spedding, "Magnetization and Electrical Resistivity of Terbium Single Crystals," *Phys Rev.*, vol. 133, no. 1 (1963), p. 158.

7. G. Green, G. Patton, and J. Stevens, "The Magnetocaloric Effects of Some Rare Earth Metals," *Adv. Cryo. Eng.*, vol. 33 (1988), p. 777.

8. L. D. Jennings, R. M. Stanton, and F. H. Spedding, "Heat Capacity of Terbium from 15 to 350 K," *J. Chem. Phys.*, vol. 27, no. 4, (1957), p. 909.

9. B. C. Gerstein, M. Griffel, L. D. Jennings, and R. E. Miller, "Heat Capacity of Holmium from 15 to 300 K," *J. Chem. Phys.*, vol. 27, no. 2 (1975), p. 394.

10. R. E. Skochdopole, M. Griffel, and F. H. Spedding, "Heat Capacity of Erbium form 15 to 320 K," *J. Chem. Phys.*, vol. 23, no. 12 (1955), p. 2258.

11. L. D. Jennings, E. Hill, and F. H. Spedding, "Heat Capacity of Thulium form 15 to 360 K," *J. Chem. Phys.*, vol. 34, no. 6 (1961), p. 2082.

12. C. B. Zimm, S. L. Kral, J. A. Barclay, G. F. Green, and G. Patton, "The Magnetocaloric Effect in Erbium," *Proceedings of 5th International Cryocooler Conference*, Dayton, OH, p. 49, (1988).

13. C. B. Zimm, J. A Barclay, H. H. Harkness, G. F. Green, and G. Patton, "Magnetocaloric Effect in Thulium," *Cryogenics* vol. 29, no. 9 (1989), p. 937.

14. C. R. Cross, J. A. Barclay, et al., "Optimal Temperature-Entropy Curves for Magnetic Refrigeration," *Adv. Cryo. Eng.*, vol. 33 (1988), p. 767.

END

DATE FILMED

11 / 15 / 90