**THERMODYNAMIC PROPERTY EVALUATION
AND MAGNETIC REFRIGERATION CYCLE ANALYSIS
FOR GADOLINIUM GALLIUM GARNET**

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CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	v
FIGURES	vii
ABSTRACT	ix
1. INTRODUCTION	1
2. PROPERTY MODELS	2
2.1 BARCLAY AND STEYERT	2
2.2 GALLAGHER	2
2.3 PRICE AND MASTRUP	2
3. DATA/MODEL COMPARISONS—NO MAGNETIC FIELD	4
3.1 HEAT CAPACITY	4
3.2 ENTROPY	4
4. DATA/MODEL COMPARISONS WITH MAGNETIC FIELD	8
5. CYCLE ANALYSIS	12
5.1 CARNOT CYCLE	12
5.2 IDEAL REGENERATIVE CYCLE	12
5.3 PSEUDO-CONSTANT FIELD REGENERATIVE CYCLE	17
6. CONCLUSIONS	22
REFERENCES	23
APPENDIX: FORTRAN COMPUTER CODE FOR MODELING MAGNETOTHERMODYNAMIC PROPERTIES OF GADOLINIUM GALLIUM GARNET	25

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FIGURES

	<u>Page</u>
1. Heat capacity with zero magnetic field	5
2. Entropy with zero magnetic field (low temperature)	6
3. Entropy with zero magnetic field (high temperature)	7
4. Comparison of magnetization models	9
5. Heat capacity at low magnetic fields	10
6. Entropy map	11
7. Limits on isentropic temperature rise and isothermal entropy drop	13
8. Sample Carnot cycles	14
9. Energy flows for Carnot cycles	15
10. Sample ideal regenerative cycles	16
11. Energy flows for ideal regenerative cycles	18
12. Sample pseudo-constant field cycles	19
13. Energy flows for pseudo-constant field cycles	20
14. Relative performance of ideal regenerative and pseudo-constant field cycles .	21
15. Entropy/temperature/magnetic field surface	35

ABSTRACT

Based on relevant material property data and previous model formulations, a magnetothermodynamic property map for gadolinium gallium garnet ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$) was adapted for refrigeration cycle analysis in the temperature range 4–40 K and the magnetic field range 0–6 T. Employing methods similar to those previously developed for other materials and temperature ranges, assessments of limitations and relative performance were made for Carnot, ideal regenerative, and pseudo-constant field regenerative cycles. It was found that although Carnot cycle limitations on available temperature lift for gadolinium gallium garnet are not as severe as the limitations for materials previously examined, considerable improvement in cooling capacity and temperature lift combinations can be achieved by using regenerative cycles if serious loss mechanisms are avoided.

1. INTRODUCTION

The basic principles of magnetic refrigeration have been recognized for many years. Recently, interest in this area has increased because of such factors as the promise of the availability of high temperature superconductors for magnet applications, the search for refrigerant alternatives to reduce ozone depletion and global warming contributions, and the emphasis on increasing energy efficiency in industrial processes.

The attractiveness of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, also called gadolinium gallium garnet or GGG, as a low-temperature magnetic refrigerant has been summarized very well by Barclay and Steyert.¹ Measurements of relevant GGG material properties have been made by Onn et al.,² Hornung et al.,³⁻⁵ Barclay and Steyert, Daudin et al.,⁶ Antyukhov et al.,⁷ Hashimoto et al.,⁸ and Dai et al.⁹ In single crystals, the effects of orientation and dislocations have been examined. For sintered material, density effects have been investigated. Notable efforts to model magnetothermodynamic properties of GGG include those of Barclay and Steyert, Daudin et al., Gallagher,¹⁰ Dai et al., and Price and Mastrup.¹¹ A number of working devices also have been constructed to provide useful refrigeration. Most of these have been of the Carnot type, but in some cases, regenerative concepts have been used.

In previous efforts, we have developed methods for modeling other magnetocaloric materials and for assessing the limitations and performance of specified regenerative and nonregenerative refrigeration cycles.^{12,13,14} In this report, we attempt to apply those methods to extend our assessments to the low-temperature range of interest for GGG, using existing models modified appropriately in recognition of relevant property data.

2. PROPERTY MODELS

2.1 BARCLAY AND STEYERT

Barclay and Steyert used the summation of two terms, one representing the lattice component and one representing the magnetic component, to describe heat capacity and entropy variations with temperature and magnetic field.¹ The lattice contribution to the heat capacity was regarded as being independent of field and proportional to the cube of temperature (in the traditional fashion of Debye-type materials at temperatures far below the Debye characteristic temperature) with the proportionality constant found by Onn et al. for temperatures up to 4.2 K (ref.2) and supported by Barclay and Steyert data up to 25 K (ref.1). Direct integration from zero to the temperature of interest was used to provide the lattice contribution to the total entropy. For zero field, the magnetic contribution to the entropy was represented by the difference in two terms based on work by Pratt et al.¹⁵ the first was the constant full magnetic entropy for the total electron orbital momentum quantum number of the material; the second was proportional to the inverse square of the ratio of the temperature of interest to the effective Néel temperature (2 K here). Differentiation of the second term was used to provide the magnetic contribution to the total heat capacity at zero field. For non-zero fields, Barclay and Steyert employed a molecular field model with associated internal fields to characterize antiferromagnetic ordering aspects of the material and to generate the relevant partition function, magnetic entropy, and magnetic heat capacity.

2.2 GALLAGHER

To represent the zero-field heat capacity up to 25 K, Gallagher used a three-term polynomial function of temperature combining an electronic contribution based on Fisher et al.³ for temperatures up to 4.2 K with a lattice contribution based on Onn et al.² up to 4.2 K and on Barclay and Steyert¹ up to 25 K. To model non-zero field effects, he used the magnetization data of Brodale et al.⁵ (for temperatures from 0.5 to 4.2 K and fields from 0.1 to 9.0 T) and Hashimoto⁸ (for temperatures from 4 to 25 K and fields from 0.3 to 9.0 T) to deduce an empirical magnetization function of temperature and field. He then integrated that function numerically from zero field to the field of interest by means of Gauss-Legendre quadrature to provide heat capacity and entropy values.

2.3 PRICE AND MASTRUP

For both zero and non-zero fields, Price and Mastrup constructed the magnetothermodynamic Gibbs function as the sum of electronic and lattice components.¹¹ The electronic contribution was deduced directly from the electronic partition function resulting from the crystal energy level structure suggested by Dai et al.⁹ For the lattice contribution, the small compressibility assumption for solids was invoked to justify approximating the Gibbs free lattice energy by the Helmholtz free lattice energy. Then the associated lattice heat capacity was represented with a variable Debye temperature form of the low temperature approximation to the Debye integral. In particular, a quadratic

temperature dependence approximation to the Debye temperature was deduced from the zero-field heat capacity data of Hornung et al.,⁴ Daudin et al.,⁶ and Dai et al. based on the apparent Debye temperature at 0 K, the minimum value for the Debye temperature, and the temperature at which the minimum occurs. Employing all these methods, we developed the explicit closed form representations for the resulting lattice integral expressions and combined them with the partition function-based electronic contribution to generate the magnetothermodynamic Gibbs function from which all remaining thermodynamic properties—including entropy, enthalpy, internal energy, Helmholtz free energy, magnetization, and total heat capacity at constant magnetic field—can be deduced. The resulting Fortran computer code is presented in the Appendix.

3. DATA/MODEL COMPARISONS—NO MAGNETIC FIELD

3.1 HEAT CAPACITY

Figure 1 shows very good agreement above 0.6 K between the Price and Mastrup model¹¹ and data from two of its indicated sources for the Debye characteristic fits, Hornung et al.⁴ and Dai et al.⁹ Since Dai et al. indicate excellent agreement between their data and those of the remaining source, Daudin et al.,⁶ for 4–30 K, Fig. 1 verifies very good agreement of the Price and Mastrup model with the zero-field heat capacity data on which it was based. In addition, the model shows comparable agreement with the single crystal cluster data of Onn et al.² above 0.6 K in Fig. 1. Excellent agreement was found between the model and the data of Antyukhov et al.⁷ over the range 4.5–30 K. Additional comparisons showed that the sintered sample data of Onn et al. were lower than the values predicted by the model below 1 K and higher above 2 K (up to 4 K), and that the single crystal data of Barclay and Steyert¹ were consistently higher than the values from the model (4–25 K). In summary, the very good low-temperature agreement with Onn et al. single crystal, Hornung et al., and Dai et al. data—plus the very good high-temperature agreement with Daudin et al., Antyukhov et al., and Dai et al. data—seem to provide substantial validation of the model under zero-field conditions.

Both the Barclay and Steyert model and the Gallagher model¹⁰ appear to offer inferior agreement with most of the zero-field data. The Barclay and Steyert model, in particular, seems to give values that are higher than the data between 0.5 and 1.0 K, lower than the data between 1 and 9 K, and higher than the data between 9 and 40 K. The Gallagher model seems to give values that are lower than the data between 0.5 and 1.0 K, about equal to the data from 2 to 6 K, and higher than the data between 6 and 40 K. Consistent with the judgment of Dai et al. that earlier studies had underestimated the effective Debye temperatures of this material, it appears that both the Barclay and Steyert model and the Gallagher model overestimate the lattice contribution to the heat capacity, which dominates for temperatures above about 10 K.

3.2 ENTROPY

By their fundamental nature, both the Price and Mastrup model and the Barclay and Steyert model give explicit values for entropy as a function of temperature with zero magnetic field. However, the polynomial nature of the Gallagher model requires the selection of a reference entropy at some finite temperature (Gallagher chose his reference entropy value to be zero at 1 K, zero field) to generate such values for a range of temperatures. For convenience in comparisons here, because the Gallagher model was based in part on data sets from Hornung et al., we have chosen to set the Gallagher model entropy value at 2 K, equal to the experimental entropy value reported by Hornung et al. at 2 K. Then all other Gallagher model values are calculated relative to this established baseline.

Figure 2 shows excellent agreement for temperatures from 0.5 to 5 K between the Price and Mastrup model and data from Hornung et al. and Dai et al. As expected, because the polynomial approximation used in the Gallagher model is based on data from the series taken by Hornung et al., the associated data/model agreement shown in Fig. 2

Fig. 1. Heat capacity with zero magnetic field.

from 1.5 to 5 K is outstanding. Below 1.5 K, the fit of the electronic component (dominant in this temperature range) of the polynomial fit breaks down, and the Gallagher model values exceed the data down to 0.5 K. The Barclay and Steyert model substantially overpredicts the data values in Fig. 2 down to about 0.75 K.

When the temperature range is extended to 40 K, as shown in Fig. 3, the superior agreement of the Price and Mastrup model with the Dai et al. data is clear. Although the Gallagher model appears to provide excellent agreement up to 10 K, it overpredicts the data for higher temperatures. The overprediction tendency of the Barclay and Steyert model decreases up to 10 K, but increases again up to 40 K. As indicated earlier, both the Gallagher and the Barclay and Steyert overprediction tendencies at temperatures above 10 K can be attributed to their overestimating the size of the lattice component, which dominates in this higher temperature range.

Fig. 2. Entropy with zero magnetic field (low temperature).

Fig. 3. Entropy with zero magnetic field (high temperature).

4. DATA/MODEL COMPARISONS WITH MAGNETIC FIELD

In his work, Gallagher¹⁰ found that the molecular field model employed by Barclay and Steyert¹ did not provide magnetization predictions that agreed well with the data of Hashimoto⁸ and Hornung et al.⁴ at low temperatures and fields. He developed an empirical formulation of magnetization as a function of temperature and field to describe the data more accurately. He judged the resulting fits to be much more accurate than other existing magnetization formulations, with only slight mismatches for temperatures below 4 K at fields above 7 T. Accounting for demagnetization effects, Dai et al.⁹ deduced energy level sequences based on three distinct eigen states which, for temperatures above 1.5 K, provided accurate representation of both their data (4–30 K, 0.1–4.0 T) and those of Hornung et al. (0.5–4.2 K, 0.1–9.0 T). Figure 4 demonstrates that the Price and Mastrup model, which incorporates these energy level sequences to form the associated electronic partition function, gives magnetization values in very good agreement with those from the Gallagher model over wide ranges in temperature and field.

Based on the information presented, it appears that the Price and Mastrup model reliably characterizes both zero-field heat capacity as a function of temperature and magnetization as a function of temperature and field. The comparisons provide a measure of confidence that the model will produce reliable predictions of the remaining magnetothermodynamic properties (especially heat capacity and entropy for finite fields) within the defined temperature and field ranges.

Additional checks were made by comparing measured heat capacities at various fields with values calculated from the model. As illustrated in Fig. 5, Dai et al. noted that, for temperatures below 4 K and fields below 2.5 T, calculated heat capacities vary somewhat from those measured by Hornung et al. They attributed those variations to degeneracies reflecting crossings in the suggested energy level map. As expected, because the crystal energy level structure suggested by Dai et al. was employed in the Price and Mastrup model,¹¹ the heat capacity data from Dai et al. agreed well with the model over the temperature range of 4 to 30 K and the field range of 0.5 to 6.0 T. The degree of agreement between the model predictions of heat capacities and the data of Barclay and Steyert and Daudin et al.⁶ was approximate, but not as good as that for the other data mentioned earlier.

A final check was made between model predictions and data for adiabatic temperature drop reported by Hashimoto et al. For two fields, 3.26 T and 4.65 T, and maximum temperatures of 10 to 30 K, the Price and Mastrup model predictions were in good agreement with the data, but the Gallagher model substantially underpredicted the adiabatic temperature drops for maximum temperatures above 20 K.

Based on the validation of the Price and Mastrup model over the ranges 4–40 K and 0–6 T, it was used to construct temperature-entropy plots for selected fields as shown in Fig. 6.

Fig. 4. Comparison of magnetization models.

Fig. 5. Heat capacity at low magnetic fields.

Fig. 6. Entropy map.

5. CYCLE ANALYSIS

The material temperature-entropy map is the starting point for analyzing candidate refrigeration cycles. Methods that we developed previously¹² were employed to examine the relative limits and performance of three types of refrigeration cycles for which both the net cooling and heat rejection processes are isothermal: the Carnot, the ideal regenerative, and the pseudo-constant field regenerative. As indicated in Fig. 7, for a given cooling temperature (4 K for the example presented here) and given maximum and minimum fields (6 T and 0 T here), limits are established by the material temperature-entropy-field map on the available isothermal entropy drop and on the available isentropic temperature rise. For a material with a map like the one shown here for GGG, the first limit establishes an upper bound on cooling capacity (135 J/kg here) for all candidate cycles. The second limit establishes an upper bound on refrigeration temperature lift (22 K here) for nonregenerative cycles like Carnot.

5.1 CARNOT CYCLE

Illustrated in Fig. 8, the Carnot cycle combines the two isothermal processes with two isentropic processes. As the heat rejection temperature rises above the cooling temperature, the available isothermal entropy change (the difference between the entropy of the low-temperature, low-field corner and the high-temperature, high-field corner of the cycle) decreases very rapidly, implying a correspondingly rapid decrease in cooling capacity (see the energy flow components of Fig. 9) until cooling capacity vanishes at a heat rejection temperature of 26 K. However, in the case of the heat rejection component, the effect of the increasing heat rejection temperature overwhelms that of the decreasing isothermal entropy change up to the heat rejection maximum at 8 K. From that point, the heat rejection falls rapidly and necessarily reaches zero to match the cooling capacity at 26 K. The work input component rises to a peak at 13 K and subsequently falls rapidly to vanish with the other two components at 26 K. By its very nature, this cycle maintains maximum cooling coefficient of performance (COP) over its entire operating range (a quite substantial range because of the outstanding properties of this refrigerant). However, if greater temperature lifts are required, alternative cycles must be considered.

5.2 IDEAL REGENERATIVE CYCLE

In theory, as explained previously, the ideal regenerative cycle can take full advantage of the field- and temperature-bounded operating region. To minimize thermal storage requirements (as illustrated by the family of cycles in Fig. 10), we have chosen to have the nonisothermal segments of the ideal regenerative cycle consist of a constant low field (actually zero field here) recovery path and a varying high field storage path that maintains a fixed horizontal separation on temperature-entropy coordinates. As the heat rejection temperature rises above the cooling temperature, the available isothermal entropy change again drops. However, the magnitude of this term—determined by the horizontal distance between the low and high field lines at the heat rejection temperature—decreases more slowly than in the Carnot example. Therefore, the ideal

Fig. 7. Limits on isentropic temperature rise and isothermal entropy drop.

Fig. 8. Sample Carnot cycles.

Fig. 9. Energy flows for Carnot cycles.

Fig. 10. Sample ideal regenerative cycles.

regenerative cycle provides cooling capacity that is greater than Carnot at every heat rejection temperature and that, in principle, never vanishes. Because the ideal regenerative cycle also maintains maximum cooling COP, its corresponding heat rejection component (peaking at a heat rejection temperature of 10 K) and work input component (peaking at 15 K) (Fig. 11) are also larger than those for the Carnot case.

5.3 PSEUDO-CONSTANT FIELD REGENERATIVE CYCLE

As pointed out in our earlier studies, if we attempt to execute a cycle comprising two isothermal and two isofield processes, for a material with a property map like that presented here, we find that the amount of heat stored in the regenerator exceeds that removed from it. This result implies that, in the absence of some additional heat sink, such a cycle does not represent steady state system operation. Therefore, to balance the heat stored in and recovered from the regenerator, the high isofield process must be terminated before the cooling temperature is reached, and a segment of adiabatic demagnetization must be added to close the cycle as shown in Fig. 12. Compared with the ideal regenerative cycle described earlier, this cycle shows (1) the same amount of heat rejected at the maximum temperature, (2) the same amount of heat stored in the regenerator, (3) a smaller amount of heat absorbed from the refrigeration load, and (4) a greater amount of work input to the system. Because the last two results imply a reduction in the cooling COP, the net effect of going from the ideal regenerative cycle to the pseudo-constant field regenerative cycle is a decrease in both refrigeration figures of merit: capacity and COP. For the present example, these decreases are attributable solely to the irreversibilities associated with imperfect regeneration.

These trends are illustrated quantitatively in Figs. 13 and 14. As the heat rejection temperature rises above the cooling temperature, the available isothermal entropy change drops less rapidly than for the Carnot case, but more rapidly than for the ideal regenerative case. Thus, the temperature lift range is extended from the Carnot value, but cooling capacity vanishes for a heat rejection temperature between 39 and 40 K (Fig. 13). For the pseudo-constant field regenerative cycle, the amount of heat rejection is equal to, and therefore the work input (peaking at a heat rejection temperature of 16 K) is greater than, the corresponding components for the ideal regenerative cycle. Consequently, the reduction in relative cooling COP is somewhat greater than in relative cooling capacity. In particular, as indicated in Fig. 14 for the conditions of the present example, the cooling COP for the pseudo-constant field cycle drops below 50% of the COP for the ideal regenerative cycle as the heat rejection temperature approaches 30 K, while the corresponding point for cooling capacity is nearly 31 K.

Fig. 11. Energy flows for ideal regenerative cycles.

Fig. 12. Sample pseudo-constant field cycles.

Fig. 13. Energy flows for pseudo-constant field cycles.

Fig. 14. Relative performance of ideal regenerative and pseudo-constant field cycles.

6. CONCLUSIONS

Based on the evidence presented here, it appears that the formulation of Price and Mastrup¹¹ is the most reliable for modeling GGG in the temperature range 4–40 K and the magnetic field range 0–6 T. When such a model is applied to Carnot cycle analysis with this material, it shows that imposed temperature lift limitations are not as severe as those found for other materials in the higher temperature ranges previously examined. However, the ideal regenerative cycle can, in principle, provide significant benefits in both temperature lift and cooling capacity for larger temperature ranges. The pseudo-constant field cycle offers smaller benefits because of the irreversibilities inherent in its characteristic regenerative processes.

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Appendix

FORTRAN COMPUTER CODE FOR MODELING MAGNETOTHERMODYNAMIC PROPERTIES OF GADOLINIUM GALLIUM GARNET


```

C   THIS PROGRAM CALCULATES THE ENTROPY OF GADOLINIUM GALLIUM
C   GARNET ACCORDING TO THE ENERGY LEVEL MODEL (WITH ZEEMAN SPLITTING)
C   DESCRIBED BY DAI ET AL. AND INTERPRETED BY PRICE AND MASTRUP OF
C   HUGHES AIRCRAFT COMPANY
C
C   IMPLICIT REAL*8(A-H,O-Z)
C   DIMENSION NU(19),TM(8),TRM(5)
C   CHARACTER*1 EL1(19),EL2(19)
C   CHARACTER*4 COOR,DAT
C   CHARACTER*10 FILENM(19)
C   COOR='HUEM'
C   DAT='.DAT'
C   PI=3.1415926536D0
C
C   DAI ZERO FIELD ENERGY LEVELS EXPRESSED AS EQUIVALENT TEMPERATURES
C
C   DATA TM/4D0,2D0,2D0,0D0,0D0,2D0,2D0,4D0/
C
C       BOHR MAGNETON (J/T)
C
C   BOHR=9.2740154D-24
C
C       AVOGADRO CONSTANT (1/MOL)
C
C   AVOG=6.0221367D23
C
C       PERMEABILITY OF VACUUM (WB/A/M)
C
C   PRMV=PI*4D-7
C
C       HUGHES VALUE FOR UNIVERSAL GAS CONSTANT (J/KMOL/K)
C
C   R=8.314510D3
C
C   HUGHES VALUE FOR FORMULA WEIGHT OF GADOLINIUM GALLIUM GARNET (KG/KMOL)
C
C   FWT=1.0123578D3
C
C   HUGHES VALUE FOR THE GAS CONSTANT FOR GADOLINIUM GALLIUM GARNET
C
C   RS=R/FWT
C
C   FORMULA MAGNETIC ION COUNT FOR GADOLINIUM GALLIUM GARNET
C
C   ENI=3D0
C
C   FORMULA INDEPENDENT OSCILLATOR COUNT FOR GADOLINIUM GALLIUM GARNET
C
C   ENS=20D0
C
C   TOTAL ELECTRON ORBITAL ANGULAR MOMENTUM QUANTUM NUMBER FOR GD3+
C
C   ZHAY=7D0/2D0
C
C       NUMBER OF MAGNETIC QUANTUM STATES
C

```

```

      N2JPLS1=ZHAY*2+1
C
C DAI VALUE FOR LANDE SPLITTING FACTOR FOR GADOLINIUM GALLIUM GARNET
C
      G=1.992D0
C
      HUGHES VALUE FOR P CONSTANT MULTIPLIER
C
      CNST=G*ZHAY*BOHR*AVOG*1D3/R
C
C HUGHES VALUE FOR SATURATION MASS MAGNETIZATION (WB M/KG)
C
      EM0=ENI*PRMV*G*ZHAY*BOHR*AVOG*1D3/FWT
C
C FISHER VALUE FOR DENSITY OF SINGLE CRYSTAL (KG/M3)
C MODIFIED TO ACCOUNT FOR REDUCED DENSITY OF SAMPLE #5
C
      RHO=7.140D3*0.89D0
      CCNST=ENS*RS*3D0
      CCCNST=4D0*PI*PI*PI*PI/5D0
      OPEN(UNIT=7,FILE='POSTR.DAT',STATUS='NEW')
      DO 400 L=1,60
C      NU(L)=L+6
C      EL1(L)=CHAR((L-1)/2+48)
C      EL2(L)=CHAR(((L+2)/2-(L+1)/2)*5+48)
C      FILENM(L)=COOR//EL1(L)//EL2(L)//DAT
C      WRITE(6,5000)COOR,EL1(L),EL2(L),DAT,FILENM(L)
C 5000 FORMAT(A5,A2,A2,A5,A12)
      H=L*0.1D0
      READ(5,*)T
C
C ***** INITIALIZE TEMPERATURE LOOP *****
C
      NPTS=73
      TMAX=40D0
      TMIN=4D0
      DT=(TMAX-TMIN)/(NPTS-1)
      DO 100 I=1,NPTS
      T=TMIN+(I-1)*DT
C
C ***** MAGNETIC COMPONENT *****
C
      HUGHES VARIABLE TRANSFORMATION
C
      TAU=1D0/T
C
      (SPHERICAL) DEMAGNETIZATION CORRECTION PER DAI
C
      READ(5,*)H
      HI=H
C      HI=0D0
C      EM2=0D0
C      DO 300 K=1,20
C      IF(K.EQ.1)GO TO 97
C      IF(K.EQ.2)HI=H
C      P=CNST*HI/T
C

```

```

C ***** INITIAL HUGHES AUXILIARY DIMENSIONLESS QUANTITIES *****
C
  SIGMA=0D0
  SUMA=0D0
  SUMB=0D0
  SUMF=0D0
  SUMG=0D0
  SUMX=0D0
C
C ***** SUMMING DO LOOP *****
C
  DO 500 N=1,N2JPLS1
C
C      MAGNETIC QUANTUM NUMBER
C
  EMJ=(N-1)-ZHAY
C
C      ELECTRONIC EXCITATION FUNCTION
C
  PHIMJ=TM(N)*TAU-EMJ*P/ZHAY
  EXPHI=1D0/DEXP(PHIMJ)
C
C      ELECTRONIC PARTITION FUNCTION
C
  SIGMA=SIGMA+EXPHI
  SUMA=SUMA+TM(N)*TAU*EXPHI
  SUMB=SUMB+EMJ*P*EXPHI/ZHAY
  SUMF=SUMF+(TM(N)*TAU)*(TM(N)*TAU)*EXPHI
  SUMG=SUMG+TM(N)*TAU*EMJ*P*EXPHI/ZHAY
  SUMX=SUMX+(EMJ*P/ZHAY)*(EMJ*P/ZHAY)*EXPHI
500  CONTINUE
C
C      FIRST ORDER PARTIAL DERIVATIVE AUXILIARY FUNCTIONS
C
  CAPA=-SUMA/SIGMA
  CAPB=SUMB/SIGMA
C
C      SECOND ORDER PARTIAL DERIVATIVE AUXILIARY FUNCTIONS
C
  CAPF=SUMF/SIGMA
  CAPG=-SUMG/SIGMA
  CAPX=SUMX/SIGMA
C
C      MAGNETIC COMPONENTS OF ENTROPY AND ENTHALPY
C
  GEEM=-DLOG(SIGMA)*ENI*RS*T
  UM=-CAPA*ENI*RS*T
  FM=-(DLOG(SIGMA)-CAPB)*ENI*RS*T
  SM=(DLOG(SIGMA)-CAPA-CAPB)*ENI*RS
  SMM=SM*FWT/1D3
  EYEM=-(CAPA+CAPB)*ENI*RS*T
C
C      MAGNETIC COMPONENT OF SPECIFIC HEAT AT CONSTANT FIELD
C
  TRM(1)=CAPF
  TRM(2)=CAPG*2D0
  TRM(3)=CAPX

```



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TRM(4)=- (CAPA+CAPB)*(CAPA+CAPB)
TRM(5)=TRM(1)+TRM(2)+TRM(3)+TRM(4)
CM=(CAPF+CAPG*2D0+CAPX-(CAPA+CAPB)*(CAPA+CAPB))*ENT*RS
CMM=CM*FWT/1D3
EM=EM0*CAPB
EM2=CAPB*ENI*RS*T*PRMV/HI
C 97 DEMAG=1D0/3D0
C EM1=(H-HI)/DEMAG/RHO
C EF=EM1-EM2
C IF(K.EQ.1)GO TO 290
C IF(DABS(EF).LT.1D-13)GO TO 310
C DER=(EF-EFO)/(HI-HIO)
C 290 HIO=HI
C EFO=EF
C IF(K.EQ.1)GO TO 300
C HI=HI-EF/DER
C 300 CONTINUE
C WRITE(6,9999)
C 9999 FORMAT(' INTERNAL MAGNETIC FIELD LOOP DID NOT CONVERGE')
C EMN=G*ZHAY*EM2/EM0
C 310 EMN=EM2*FWT/ENI/AVOG/BOHR/PRMV/1D3
C RSUS=HI*ENI*PI*4D0*1D3/EM2/FWT/1D6
C EMG=EM2/PRMV
C
C ***** LATTICE COMPONENT MODELS *****
C
CALL HUCSLT(T,CL,CTINTT,CTINTB,CINTT,CINTB)
CLM=CL*FWT/1D3
CT=CM+CL
DIFCT=CTINTT-CTINTB
DIFC=CINTT-CINTB
GEEL=CCNST*CCCNST*(DIFC-T*DIFCT)
UL=CCNST*CCCNST*DIFC
FL=CCNST*CCCNST*(DIFC-T*DIFCT)
SL=CCNST*CCCNST*DIFCT
SLM=SL*FWT/1D3
SLN=SLM*1D3/R
EYEL=CCNST*CCCNST*DIFC
GEET=GEEM+GEEL
UT=UM+UL
FT=FM+FL
ST=SM+SL
EYET=EYEM+EYEL
CTM=CT*FWT/1D3
CTM=CLM+CMM
CTG=CT/1D3
CTB=CTM*1D3/R/3D0
CTN=CTM*1D3/R
STM=ST*FWT/1D3
SN=STM*1D3/R
IF(T.EQ.1D0)EYE1=EYET
HM=(EYET-EYE1)*FWT/1D3
HT=H/T
8000 FORMAT(F6.1,F8.2,F7.1,2F8.1)
1000 FORMAT(F6.1,F5.1,F9.5)
WRITE(6,1000)T,H,SN
WRITE(7,1000)T,H,SN

```

```

2000 FORMAT(6F9.4)
100 CONTINUE
400 CONTINUE
    CLOSE(UNIT=7)
    STOP
    END

    SUBROUTINE HUCSLT(T,CL,CTINTT,CTINTB,CINTT,CINTB)
C
C *** LATTICE COMPONENT MODEL-HUGHES DEBYE WITH VARIABLE DEBYE TEMP ***
C INPUT IS TEMPERATURE; OUTPUTS ARE LATTICE SPECIFIC HEAT AND INTEGRALS
C
    IMPLICIT REAL*8(A-H,O-Z)
C
    ZERO K AND MIN DEBYE TEMPS AND TEMP AT MINIMUM
C
    R=8.314510D3
    FWT=1.0123578D3
    RS=R/FWT
    ENS=20D0
    THD0=520D0
    THDMIN=400D0
    TDMIN=30D0
    CALL TDQ0MD(T,THD0,THDMIN,TDMIN,THD,A,B,C)
C
C LATTICE SPECIFIC HEAT USING LOW TEMP DEBYE INTEGRAL APPROXIMATION
C
    CCNST=ENS*RS*3D0
    X=THD/T
    CL=CCNST*DEBLT(X)
C
C ***** LATTICE ENTROPY FROM EXPLICIT INTEGRATION *****
C
    TBASE=0D0
    CALL TEG(T,A,B,C,CTINTT,CINTT)
    CALL TEG(TBASE,A,B,C,CTINTB,CINTB)
    RETURN
    END

    SUBROUTINE TDQ0MD(T,THD0,THDMIN,TDMIN,THD,A,B,C)
C
C QUADRATIC FIT MATCHING ZERO K, MIN, AND ZERO DERIVATIVE AT MIN
C
    IMPLICIT REAL*8(A-H,O-Z)
    A=THD0
    B=(THDMIN-THD0)*2D0/TDMIN
    C=(THD0-THDMIN)/TDMIN/TDMIN
    THD=QUAD(T,A,B,C)
    RETURN
    END

    FUNCTION QUAD(T,A,B,C)
    IMPLICIT REAL*8(A-H,O-Z)
    QUAD=A+B*T+C*T*T
    RETURN
    END

```

```

      FUNCTION DEBLT(X)
C
C ***** LOW TEMPERATURE DEBYE FUNCTION APPROXIMATION *****
C
      IMPLICIT REAL*8(A-H,O-Z)
      PI=3.1415926536D0
      CCCNST=4D0*PI*PI*PI*PI/5D0
      DEBLT=CCCNST/X/X/X
      RETURN
      END

      SUBROUTINE TEG(T,A,B,C,CVOVRT,CV)
      IMPLICIT REAL*8(A-H,O-Z)
C
C *** INVERSE QUADRATIC INTEGRATOR BASED ON CRC #98,#87,#90, *****
C
      X=A+B*T+C*T*T
      Q=4*A*C-B*B
C
C      FIRST TERM OF INTEGRAL BASED ON CRC #98
C
      TM1=-T/C/X/X/3D0
      TM4=-T*T/C/X/X/2D0
C
C      FIRST TERM OF FIRST SUBINTEGRAL BASED ON CRC #87
C
      TM21=-(A*2D0+B*T)/Q/X/X/2D0
C
C      FIRST SUB-SUB-SUBINTEGRAL BASED ON CRC #87
C
      TEG211=2D0/Q**0.5D0*DATAN((C*T*2D0+B)/Q**0.5D0)
C
C      FIRST SUB-SUBINTEGRAL BASED ON CRC #90
C
      TEG21=(C*T*2D0+B)/Q/X+C*2D0/Q*TEG211
C
C      FIRST SUBINTEGRAL BASED ON CRC #87
C
      TEG2=TM21-B*3D0/2D0/Q*TEG21
C
C      SECOND TERM OF INTEGRAL BASED ON CRC #98
C
      TM2=-B/C/3D0*TEG2
      TM5=A/C*TEG2
C
C      FIRST FACTOR OF FIRST TERM OF SECOND SUBINTEGRAL BASED ON CRC #91
C
      TM311=(C*T*2D0+B)/Q
C
C      SECOND FACTOR OF FIRST TERM OF SECOND SUBINTEGRAL BASED ON CRC #91
C
      TM312=1D0/2D0/X/X+C*3D0/Q/X
C
C      FIRST TERM OF SECOND SUBINTEGRAL BASED ON CRC #91
C
      TM31=TM311*TM312
C

```

```

C      SECOND SUB-SUBINTEGRAL BASED ON CRC #87
C
C      TEG31=TEG211
C
C      SECOND SUBINTEGRAL BASED ON CRC #91
C
C      TEG3=TM31+C*C*6D0/Q/Q*TEG31
C
C      THIRD TERM OF INTEGRAL BASED ON CRC #98
C
C      TM3=A/C/3D0*TEG3
C
C      TOTAL INTEGRAL
C
C      CVOVRT=TM1+TM2+TM3
C      CV=TM4+TM5
C      RETURN
C      END
C
C      SUBROUTINE MUCS(T,THD,CL)
C ***** LATTICE COMPONENT MODEL--DEBYE WITH VARIABLE DEBYE TEMP *****
C      INPUT IS TEMPERATURE; OUTPUT IS LATTICE SPECIFIC HEAT
C
C      IMPLICIT REAL*8(A-H,O-Z)
C      R=8.314510D3
C      FWT=1.0123578D3
C      RS=R/FWT
C      ENS=20D0
C
C      DEBYE TEMPERATURE FUNCTION
C
C      ZERO K AND MIN DEBYE TEMPS AND TEMP AT MINIMUM
C
C      THD0=520D0
C      THDMIN=400D0
C      TDMIN=30D0
C      THD=TDQ0MD(T,THD0,THDMIN,TDMIN)
C      A=567.942D0
C      B=-13.8324D0
C      C=0.360666D0
C      D=-0.00269333D0
C      THD=520D0-5.2993D0*T
C      IF (T.GT.20D0)THD=POLY(T,A,B,C,D)
C      CCNST=ENS*RS*3D0
C      X=THD/T
C      CL=CCNST*DEBAT(X)
C      RETURN
C      END
C
C      FUNCTION POLY(T,A,B,C,D)
C      IMPLICIT REAL*8(A-H,O-Z)
C      POLY=A+B*T+C*T*T+D*T*T*T
C      RETURN
C      END
C
C      FUNCTION DEBAT(X)

```

```

C
C *** "EXACT" DEBYE HEAT CAPACITY FUNCTION (FULL INTEGRAL EVALUATION) ***
C
      IMPLICIT REAL*8(A-H,O-Z)
C
      INITIALIZE BEGINNING OF INTEGRATION
C
      A=0D0
      FA=0D0
      TOTNT=0D0
      B=X
      FB=DEXP(B)*B*B*B*B/(DEXP(B)-1D0)/(DEXP(B)-1D0)
      TEGO=0D0
      DO 100 I=1,16
C
C      SET NUMBER OF INTEGRATION INTERVALS
C
      N=2**I
C
C      FIND SIZE OF INTEGRATION INTERVALS
C
      DELX=(B-A)/N
C
C      INITIALIZE INTEGRAL SUMMATION
C
      S=0D0
      DO 200 J=1,N-1
      X=A+J*DELX
      IF(X.GE.709.78271259338403D0)GO TO 200
      FX=DEXP(X)*X*X*X*X/(DEXP(X)-1D0)/(DEXP(X)-1D0)
      S=S+FX
C
      WRITE(6,7000)J,I,K,L,X,FX,S
7000  FORMAT(4I6,3D15.5)
200  CONTINUE
      TEG=DELX*(S+(FA+FB)/2D0)
      CHNG=(TEG-TEGO)/TEG
      TEST=(TEG-TEGO)/(TOTNT+TEG)
      WRITE(6,226)I,A,B,FA,FB,TEG
226  FORMAT(13,2F10.6,2D15.5,D20.10)
C
C      DETERMINE IF NUMBER OF INTERVALS IS ADEQUATE
C
      IF(DABS(TEST).LT.1D-9)GO TO 110
      TEGO=TEG
100  CONTINUE
      WRITE(6,9900)
9900  FORMAT(' INTEGRAL ITERATION DID NOT CONVERGE')
110  TOTNT=TOTNT+TEG
      DEBAT=TOTNT*3D0/X/X/X
      RETURN
      END

```

material: gadolinium gallium garnet ($Gd_3Ga_5O_{12}$)
 model: Price-Mastrup
 formula weight: 1012.3578
 formula magnetic ion count: 3
 formula independent oscillator count: 20
 total electron orbital angular momentum quantum number: $7/2$
 Lande splitting factor: 1.992
 zero magnetic field level energy constants:
 magnetic quantum number equivalent temperature
 $\pm 1/2$ 0 K
 $\pm 3/2$ 2 K
 $\pm 5/2$ 2 K
 $\pm 7/2$ 4 K
 Debye value fit: quadratic
 low temperature Debye limiting value: 520 K
 minimum Debye value: 400 K
 temperature of minimum Debye value: 30 K

Fig. 15. Entropy/temperature/magnetic field surface.

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