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Magnetic cooling near Curie temperatures above 300 K

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Selection of materials and expected magnetocaloric effects are discussed for magnetic cooling applications at elevated temperatures (400–800 K). Various considerations result in the selection of rare earth-transition metal compounds such as Sm₂Fe_{17-x}Co_x for this task. These materials offer a wide range of suitable magnetic ordering temperatures as a function of x. They also show relatively high effective magnetic moments per volume. Molecular field models are developed for analytically predicting entropy changes at and above the ordering temperature. Concomitant adiabatic cooling ΔT is accordingly computed for these compounds near the ordering temperatures. It is found that for a family of compounds ΔT values increase somewhat with increasing ordering temperatures due to the decreasing influence of the lattice heat capacity at higher temperatures. Adiabatic cooling of $\Delta T = -7.5$ K at 70 kOe to $\Delta T = -9.2$ K at 70 kOe is predicted for materials Y₂Fe_{17-x}Co_x near their Curie points of 300 and 600 K, respectively (corresponding to materials with $x \sim 0.1$ to $x \sim 0.3$). This compares with similar predictions for Gd of $\Delta T = -12.6$ K at 70 kOe near 300 K. However, on a per volume basis, the isothermal heat pumping capacities $T\Delta S$ at $T_i = T_c$ for initial fields of 70 kOe are 7.5, 12.1, and 15.2 cal cm⁻³ for Gd ($T_i = 300$ K), $Y_2 Fe_{17-x} Co_x$, and $Sm_2 Fe_{17-x} Co_x$ (both at $T_i = 600$ K), respectively. These intermetallics are, therefore, on a per volume basis, predicted to work over a range of temperatures with efficiencies higher than the efficiency of Gd near room temperature.

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I. INTRODUCTION

Strong magnetocaloric effects occur upon exposure of a magnetic material to external magnetic fields near the magnetic ordering temperature T_c of the material. This magnetocaloric effect can be made use of in refrigeration applications. Current interest for noncryogenic application centers around room temperature, $^{1-5}$ with elemental Gd a leading candidate for utilization. The benefits of magnetic materials in thermodynamic cycles have been summarized by Brown. A primary advantage over a gas process is the much larger entropy density in a solid near T_c , some two orders of magnitude greater than with a gas. Efficiency of the magnetic cycle can approach that of the Carnot value.

In this work, we shall consider extension of the temperature range to higher temperatures, and consider specifically materials with T_c near 600 K. A discussion of the relative merits in the choice of materials for cooling near Curie temperatures will include consideration of suitable Curie temperatures, magnetic moments, and entropy characteristics. Predictive approximate formalisms are developed to obtain criteria for suitable materials, with the emphasis on the region of maximum effects near T_c , and to compare with the Gd standard. We consider both adiabatic cooling and isothermal heat pumping capabilities. Although some of the specific examples given are for materials with T_c near 600 K, the model calculations are generally valid for materials with T_c at or below room temperature.

II. CURIE TEMPERATURES AND MAGNETIC MOMENTS

Although the highest moments are obtained with elements of the rare earth group R, the highest Curie tempera-

tures of rare earth elements and compounds without transition metals (achieved with Gd, $T_c = 298$ K, and Gd₅Si₄, T_c = 335 K) are insufficient for the purposes under consideration. Combinations of rare earths and transition metals T are therefore considered. In these compounds⁶ the relatively high ordering temperatures of T metals (e.g., Co, $T_c \approx 1400$ K) can be lowered in measured steps. Data for a selected number of R-T compounds are presented in Table I for the sake of comparison. Magnetic moments are most favorable around the composition Y₂Fe₁₇. It appears that this composition⁶ is very responsive in T_c to small substitutions according to Y₂Fe_{17-x}Co_x or Y₂Fe_{17-x}Ni_x. This makes these compound series especially attractive for utilization covering a wide variety of ordering temperatures. We have therefore chosen these materials as model substances for calculational approaches to the problem of magnetic cooling near elevated magnetic ordering temperatures.

III. ENTROPY CALCULATIONS

For an adiabatic process, the initial (i) and final (F) entropies are equal. Thus,

$$S_{m}^{F} + S_{l}^{F} + S_{e}^{F} = S_{m}^{i} + S_{l}^{i} + S_{e}^{i}, \qquad (1)$$

where the subscripts m, l, and e refer to the magnetic, lattice, and conduction electron terms, respectively. It will be shown that in many cases analytic solutions can be obtained for the various terms involved. This obviates the need for repetitive iterative calculations, and more importantly, gives insight into the importance of factors entering the relationships.

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TABLE I. Magnetic characteristics of some selected materials. The moment n_s is the saturation moment per formula unit at 4.2 K. V_a is the average atomic volume. f_r denotes the volume entropy change coefficient at T_c as seen in Eqs. (24) and (25), $(q/MV_a)(gJ)^{2/3}$, normalized to Gd. gJ is taken as the moment per T ion.

Compounds	$T_c(\mathbf{K})$	$n_s(\mu_B)$	$V_a(\mathring{\mathbf{A}}^3)$	f,	Ref.
YFe ₃	569	5.22	15.6	0.62	6
Y_2Fe_{17}	324	34.9	13.6	0.95 (1.22) ^a	6,17
$Y_2(Co_{0.3}Fe_{0.7})_{17}$	600	38.1	13.5	1.01	6,17
Ce ₂ Fe ₁₇	238	29.7	13.6	0.85	6
Sm ₂ Fe ₁₇	368	37.9	13.8		6,18
YCo ₃	306	1.65	14.6	0.31	6
Y_6Fe_{23}	481	43.1	15.2	0.71	6
Y_6Mn_{23}	486	12.4	16.7	0.28	6
Gd	298	7.0	32.7	1.00	19
Gd ₅ Si ₄	336	36.2	23.8	0.78	20
Fe	1043	2.2	11.7	1.29	19
γFe ₄ N	761	8.9	10.9	1.11	21
Fe_2B	1013	3.87	9.2	1.00	22
Fe ₃ C	483	5.64	9.7	1.05	23
$a-Fe_{0.8}B_{0.2}^{b}$	660	1.73	11.1	1.08	24,25

^aJ from paramagnetic data.

A. Electronic entropy

The electronic entropy is given by $S_e = \gamma T$, with γ the electronic specific heat coefficient given per mole. This entropy contribution is least important. The following values are representative for rare earth¹ and transition metals,⁷ respectively:

$$\gamma$$
(cal/mole K²)
Gd: 2.6×10⁻³;
Fe: 1.2×10⁻³.

For R_2Fe_{17} , we assume its γ/m (where m is the number of atoms per molecule) is equal to that of Fe.

B. Lattice entropy

The lattice entropy is given by⁸

$$S_L = mR \left[-3 \ln(1 - e^{-\theta_D/T}) + 4D \left(\frac{\theta}{T}\right) \right], \qquad (2)$$

where R is the gas constant and θ_D the Debye temperature. D(x) is tabulated in Morse, and can be expanded in a power series to $\theta_D/T \equiv x = 2$ as

$$D(x) = 1.000 - 0.375x + 0.050x^2 - 0.0011x^3$$
 (3)

to about 0.1% accuracy.

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Expanding both the exponential and ln terms to fourth power, we find complete cancellation of the linear term and partial cancellation elsewhere:

$$\frac{S_L}{mR} = 4 - 3 \ln x + 0.0750x^2 - 0.0044x^3 + 0.00105x^4.$$
 (4)

Of interest to the present work is the change in entropy with temperature,

$$\Delta S_L \approx 3mR \, \frac{\Delta T}{T} \,.$$
 (5)

This approximation is accurate to about 1% at x = 0.5, 5%

at x = 1, and 10% at x = 1.5. Debye temperatures of interest include the following^{1,10}:

$$\theta_D(\mathbf{K})$$

Gd: 172;

Fe: 467;

Thus, for temperatures of interest (~ 600 K), $\theta_D/T < 1$ and the above approximation holds well.

C. Magnetic entropy

The defining relationship for magnetic entropy is given v

$$S_m = -\left(\frac{\partial F}{\partial T}\right)_H,$$

with

$$F_{\rm ion} = -kT \ln z, \qquad (6)$$

and z the partition function. Computations are performed within the molecular field theory. All the results presented below were checked by comparison with results obtained by using this exact relationship. A useful approximation can be obtained from a different formula:

$$\Delta S_m = S_m - S_{mo} = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH,\tag{7}$$

along with Curie-Weiss behavior well above T_c ,

$$M_{\rm ion} = \frac{p_e^2 \,\mu_B^2 H}{3k \, (T - \theta)} \,. \tag{8}$$

Thus

$$\Delta S_m = -\frac{qR}{6} \left(\frac{p_e \,\mu_B H}{k \, (T - \theta)} \right)^2, \tag{9}$$

where p_e is the effective moment per ion, $\theta \equiv T_c$ the Weiss temperature, and q the number of magnetic ions per mole.

Accordingly, Brown¹ noted the apparent efficacy of large effective moments per atom. While this will be shown to be a good approximation under certain assumptions, care has to be taken since this Curie-Weiss approximation is found to be valid for only small values of the argument. An important relationship for later discussion can be obtained from the above and the saturation behavior,

$$\sigma_m = \frac{M_{\text{ion}}}{M_s} = \frac{g(J+1)\mu_B H}{3k(T-\theta)},$$
(10)

with $M_s = gJ\mu_B$. Thus,

$$\Delta S_m = -\frac{3}{2} qR \frac{J}{J+1} \sigma_m^2 . \tag{11}$$

From calculations with the defining relationship (6) above, we find that Eq. (11) has a much wider validity than the Curie-Weiss origin would imply. For Gd, the approximate value ΔS_m calculated by Eq. (11) is about 5% smaller in magnitude than the exact value for $\sigma_m^2 = 0.2$, with the error essentially proportional to σ_m^2 for values of σ_m^2 to 0.4.

For the magnetic entropy in zero applied field below T_c , ΔS_m^F , we now can use the molecular field theory prediction for σ_m , 11

^b Allied Chemical METGLAS® 2605 amorphous alloy.

TABLE II. Magnetocaloric effects as a function of initial temperature T_i for various materials, assuming field of 70 kOe.

Material ^a	T_i (K)	θ (K)	$-\Delta S_m^i$ (cal mo ⁻¹ K ⁻¹) ^b	$-T\Delta S_{m}^{i}$ (cal cm ⁻³) ^b	$-\Delta T(\mathbf{K})^c$
Gd	300*	300	0.49	7.5	12.6
"Gd"	600* 660 680 700	600 600 600	0.31 0.13 0.073 0.046	9.5	15.0 11 6 4
Y ₂ Fe ₁₇ "Y ₂ Fe ₁₇ "	300* 600*	300 600	4.9 3.1	9.5 12.1	7.5 9.2
"Sm ₂ Fe ₁₇ "	600*	600	4.0	15.2	10.5

^{*} Materials in quotation marks denote hypothetical materials with assumed θ . For the Fe base materials, properties assumed can be achieved in compound series R_2Fe_{17} $_xCo_x$. θ values for Gd and Y_2Fe_{17} were approximated for comparison.

$$\sigma_m^2 = \frac{10}{3} \frac{(J+1)^2}{(J+1)^2 + J^2} \left(1 - \frac{T}{T_c}\right),\tag{12}$$

to find

$$\Delta S_m^F = \frac{5qRJ(J+1)}{[J^2 + (J+1)^2]} \frac{\Delta T}{T_c},$$
(13)

with $\Delta T = T - T_c$. For Gd, the error in the approximate value σ_m^2 calculated by Eq. (12) is essentially proportional to σ_m^2 , and amounts to about +6% for $\sigma_m^2 = 0.2$.

Additionally, we find that the magnetic entropy at T_c as a function of field can be calculated analytically. Kouvel and Fisher 12 have expanded the Brillouin solution of magnetization versus field near T_c , and by reversion of the power series obtain near T_c

$$H = (T - T_c) \frac{3k}{g(J+1)\mu_B} \sigma_m + (kT/r\mu_B)\sigma_m^3 + \cdots, \quad (14)$$

where r is given as a polynomial in J. This is, of course, equivalent to the Belov-Arrott relationship used in determining T_c . For small σ_m , one obtains Eq. (10). At $T=T_c$, we can solve for σ_m and obtain

$$\sigma_m = \left(\frac{10}{9} \frac{g(J+1)^3}{[(J+1)^2 + J^2]} \frac{\mu_B}{kT_c} H\right)^{1/3}.$$
 (15)

Then, from Eq. (11), we have at T_c

$$\Delta S_m = -\frac{3}{2} qR \frac{J(J+1)}{[J^2 + (J+1)^2]^{2/3}} \left(\frac{10}{9} \frac{g\mu_B H}{kT_c}\right)^{2/3}. \quad (16)$$

The error in the approximate value ΔS_m calculated by Eq. (16) increases for large J, large H, and low T_c , and is approximately proportional to σ_m^2 . Of the calculations considered in Table II, the worst-case error occurs for Gd at 70 kOe applied field and 300 K, with the magnitude of the approximate ΔS_m some 6% greater than for the exact calculation.

The quantity

$$p(J) \equiv \frac{J(J+1)}{[J^2 + (J+1)^2]^{2/3}},$$
(17)

can be represented very well (to $\pm 3\%$, $1/2 \le J \le 8$) by $p(J) = (2/3) J^{2/3}$. Thus, at T_c ,

$$\Delta S_m \approx -1.07 qR \left(\frac{g\mu_B JH}{kT_c}\right)^{2/3}.$$
 (18)

One should compare this 2/3 power law dependence with Eq. (9), the high temperature Curie law showing quadratic behavior in ΔS_m . Thus the magnitude of J is not very important in determining magnetocaloric effects at the technologically important temperature T_c .

D. Magnetocaloric relations

1. $T_i = T_c$

We can now perform some calculations of expected magnetocaloric effects. From Eq. (1), we have

$$\Delta S_m^T = \Delta S_m^F + \Delta S_I^F + \Delta S_e^F. \tag{19}$$

At $T_i = T_c$,

$$\Delta S_{m}^{i} = \left\{ \frac{5J(J+1)qR}{[J^{2} + (J+1)^{2}]T_{c}} + \frac{3mR}{T_{c}} + \gamma \right\} \Delta T, \quad (20)$$

with ΔS_m^i given by Eq. (16).

For adiabatic conditions

$$\Delta T = \Delta S_m^i = \left\{ \frac{5J(J+1)qR}{[J^2+(J+1)^2]T_c} + \frac{3mR}{T_c} + \gamma \right\}.$$
 (21)

Note that ΔT is proportional to ΔS_m^i in this linearized equation. We find from comparison with Brown's experimental data on Gd at T_c that ΔT is indeed proportional to $H^{2/3}$. Thus, the expected response is found for the well-localized Gd moment. For more itinerant materials, an example would be Ni (Ref. 12) where we can infer $\Delta S_m^i \propto H^{1/2}$ at T_c .

Results for ΔT obtained according to Eq. (21), given in Table II, with asterisks, indicate that for compounds in $Y_2Fe_{17-x}Co_x$ the magnitudes (values at T_c are calculated corresponding to near maximum) increase with T_c , but stay below those for Gd. However when isothermal heat pumping capacities $\Delta Q \equiv -T\Delta S_m^i$ at $T_i = T_c$ for initial fields of 70 kOe are calculated on a per volume basis, materials in $Y_2Fe_{17-x}Co_x$ are actually better than Gd (e.g., 7.5 cal cm⁻³ for Gd vs 9.5 cal cm⁻³ for Y_2Fe_{17} , as shown in Table II). The packing density can overrule the weaker $(gJ)^{2/3}$ dependence seen in Eq. (18); Fe has 2.8 times the packing density of Gd. A further enhancement is possible through substitution for Y by other magnetic rare earths. One achieves here a favorable loss of S_m due to the molecular field H_m between R and T.

By comparing with previous experimental ΔT data of Hashimoto et al.,⁴ we find reasonably good agreement. For 20 kOe applied field on Gd near T_c , the maximum observed $|\Delta T|$ obtained by adiabatic demagnetization was about 5.0 K (the correction for demagnetizing field is unknown). We calculate a predicted $|\Delta T| \approx 5.4$ K, using Table I and the

^b Isothermal response. Rows with asterisks are calculated using Eq. (16), others with Eq. (9).

^c Adiabatic cooling response; rows with asterisks are calculated using Eq. (21), others with Eq. (22).

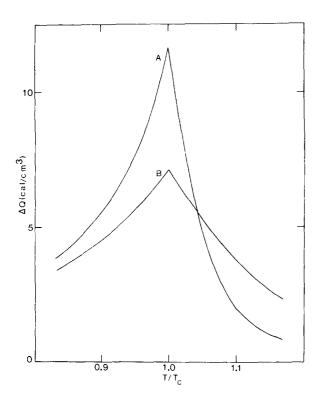


FIG. 1. Isothermal heat pumping capacities $\Delta Q \equiv -T(S_m^i - S_m^F)$ for an initial field of 70 kOe: (A) $Y_2 \text{Fe}_{17-x} \text{Co}_x$ with $T_c = 600 \text{ K}$, (B) Gd with $T_c = 300 \text{ K}$.

 $H^{2/3}$ power law for ΔS_m^i . Also their numerically calculated $|\Delta S_m|$ at T_c agrees to within a percent or so of our value. Brown has done an adiabatic magnetization experiment on Gd, and obtained a numerical calculation theoretical temperature rise of 15 K at T_c for a field of 70 kOe. We calculate an expected rise of 21 K (ΔS_m^F is zero under these conditions). The difference appears to lie in the value of σ_m at 70 kOe. We calculate $\sigma_m = 0.436$ (by the exact method) whereas Brown calculates $\sigma_m = 0.37$. Since $\Delta S_m^i \propto \sigma_m^2$, the two calculated ΔT values are in good agreement if Brown's value is corrected.

The fact that cooling is somewhat more pronounced at elevated temperatures compared to 300 K can be seen as a result of the terms in Eq. (21). The dominant lattice and final magnetic terms in the denominator decrease as T_c^{-1} , while the numerator decreases only as $T_c^{-2/3}$ [Eq. (18)]. As an example of the typical magnitudes of the terms in the denominator of Eq. (21), we consider $Y_2 \text{Fe}_{17-x} \text{Co}_x$ with T_c = 600 K. The relative sizes of the lattice, final magnetic, and electronic contributions are 1.00, 0.66, and 0.12, respectively. This leads to an interesting facet of the adiabatic response: the maximum adiabatic cooling $|\Delta T|$ occurs when $T_i > T_c$. Although $|\Delta S_m^i|$ is reduced for $T_i > T_c$, the final magnetic term ΔS_m^F is zero until T reaches T_c . For example, with $Y_2 \text{Fe}_{17-x} \text{Co}_x$, $T_c = 600 \text{ K}$, H = 10 kOe, we find the maximum $|\Delta T|$ at $T_i \approx 603$ K which is some 15% greater than the value at $T_i = T_c$.

2. T_i≥T_c

For $T \gg T_c$, we use Eqs. (9) and (19) to obtain

 $\Delta T = \Delta S_m^i / (3mR/T_c + \gamma)$ or

$$\Delta T = -\frac{qR}{6} \left(\frac{p_e \,\mu_B H}{k \, (T - \theta)} \right)^2 / (3mR \,/T_c + \gamma) \,. \tag{22}$$

Some values calculated accordingly are shown in Table II. These are only in fair agreement compared with values calculated with ΔS_m^i obtained from Eq. (6). For example, the approximate relationship Eq. (22) gives $\Delta T = -11$ K for "Gd" with 70 kG at $T_i = 660$ K, whereas the exact determination gives $\Delta T = -7$ K.

It is also of interest to note that the curve shape of ΔT vs T_i is predicted to be rather different for Gd vs Fe-based materials. The dependence of ΔT on p^2 from Eq. (22) for a paramagnet indicates a less favorable situation for $T_i \gg T_c$ for Febased materials (compared with Gd) than obtained from Eq. (21) for $T_i = T_c$. However, as the heat pump will operate in the temperature region near maximum cooling effects, this should not be of great importance.

3. General cooling capabilities

Finally, we consider the cooling capacities as determined by the exact relationship (6). The solution for the magnetization in terms of the Brillouin function was obtained numerically by a Newton-Raphson technique, and the resulting entropy calculated from the value of $(H+H_m)/T$, where the molecular field H_m is assumed proportional to σ_m . In Fig. 1, the isothermal heat pumping capacities $\Delta Q = -T(S_m^i - S_m^F)$ are shown for two materials as a function of T/T_c , with the initial field 70 kOe. Curve A represents a compound in the pseudobinary series $Y_2 Fe_{17-x} Co_x$ with a T_c of 600 K, and curve B elemental Gd with $T_c = 300$ K. The volume cooling capability of the $Y_2 Fe_{17-x} Co_x$ is substantially greater than that for Gd, for T/T_c less than 0.9 to T/T_c about 1.04.

E. Additional considerations

In the calculation for $Y_2 Fe_{17-x} Co_x$, for J we used the value J=1.5 as obtained for $Y_2 Fe_{17}$ from its Curie–Weiss behavior with $p=4.0~\mu_B$. If one instead chooses J as determined from the saturation moment n_s at 4.2 K, $J \approx 1.0$. At $T_i = T_c$ this makes relatively little difference because of the $J^{2/3}$ dependence of ΔS_m^i . Moreover, for higher values of T_c in the pseudobinary series, we expect J as determined by the saturation behavior to approach that from the paramagnetic behavior. I^3

For a calculation of ΔT of "Sm₂Fe₁₇" at $T_i = T_c$, we assumed free-ion Sm behavior coupling magnetically to the Fe sublattice, with the exchange coupling constant $\mu_B H_e \sigma_{\rm Fe}$ obtained ¹⁴ from an analysis of the low temperature dependence of anisotropy in some Sm₂Fe_{17-x}Co_x. An iterative calculation was performed on ΔT ; ΔS_m^i for Sm was approximated by Eq. (11). The Sm moment is known to be coupled antiferromagnetically with Fe in this temperature region; however, the coupling of Sm to the external field is essentially zero.

A possible problem for achieving maximum ΔQ in applied fields is posed by the effect of crystalline anisotropy on

 θ . The observed values of the Curie-Weiss θ will vary dependent on measurement axis. This will be markedly apparent for materials with anisotropic rare earths. For Y_2Fe_{17} , we calculate the difference $\theta_a-\theta_c$ by comparing two equations, one¹⁵ referring $\theta_a-\theta_c$ to the crystal field parameter B_2^0 , and another¹⁶ referring B_2^0 to the low temperature anisotropy K. We find

$$\theta_a - \theta_c = \frac{(2J - 1)(2J + 3)K}{10J(J - \frac{1}{2})Nk},$$
 (23)

where N is the number density of Fe. For Y_2 Fe₁₇, at low temperature $K \approx -25 \times 10^6$ erg cm⁻³.¹⁷ Thus $\theta_a - \theta_c \approx -2.7$ K. This is not very significant, as noted earlier. Moreover, Co substitution reduces K to zero at about x = 0.45.

Bulk anisotropy from anisotropic rare earths can be nominally reduced to zero by suitable mixtures of Sm (uniaxial anisotropy) and Nd (planar anisotropy). This technique was applied in the U. S. Naval RFe₂ transducer program. However, with values of $|\theta_a - \theta_c|$ as high as 50 K for RT_x materials, fairly precise Sm to Nd ratios must be maintained to ensure consistent elimination of the anisotropy. Below T_c , this will also reduce the concomitant hysteresis effects due to domain wall pinning.

For ease of comparison of various materials, we show how to calculate the relative heat pumping capacity ΔQ per cm³ in terms of standard low temperature saturation magnetization parameters. We use Eq. (18) and convert to volume units. Two equivalent relationships are then

$$\Delta S (\text{cm}^{-3}) \propto \left(\frac{qM_g^2}{mV_a}\right)^{1/3} \left(\frac{H}{T_c}\right)^{2/3},$$
 (24)

$$\Delta S (\text{cm}^{-3}) \propto 441 \left(\frac{q}{mV_a}\right) (gJ)^{2/3} \left(\frac{H}{T_c}\right)^{2/3}$$
 (25)

 M_g is the magnetization at 0 K in gauss (emu cm⁻³), m is the number of atoms per molecule of which q are magnetic and carry moment gJ, and V_a is the average atomic volume (the molecular volume divided by m). The leading number 441 in Eq. (25) is the conversion factor between the two equations [given by $(\mu_B \text{ Å}^3 \text{ cm}^{-3})^{2/3}$]. For comparison, the value of $(qM_g^2/mV_a)^{1/3}$ for Gd is 49.3 G^{2/3} Å⁻¹. Relative values of this factor f, are tabulated in Table I, normalized to that for Gd. The use of the approximation $p(J) = (2/3)J^{2/3}$ produces

an extra 2% reduction in f_r for the transition metal compounds.

As can be seen from Table I, some improvement in relative cooling power f_r , occurs from Gd to Fe. A few iron-based materials listed in the table also show promise, with the thinness of the amorphous materials advantageous for maximum heat transfer. However, for ease of preparation, chemical stability, and ease of variation of T_c with chemical substitution, the $Y_2 Fe_{17-x} Co_x$ materials seem a good choice

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