

suring the magnetization as a function of applied field from 260 to 320 K at each 10 K interval.

**[0040]** For each loop, the field was cycled from zero to 5 T and back to zero. The hysteretic loss values summarized in Table 22 of FIG. 9 provide a quantitative comparison for the metal additive-free alloy and alloys with the Fe metal additive. These hysteresis loss values were determined by computing the area inside each magnetization versus field loop. From this comparison, it can be clearly seen that the addition of about one atom percent iron to the  $Gd_5Ge_2Si_2$  alloy resulted in a reduction of the hysteresis losses by more than 90 percent compared to the alloy without any metal additives.

**[0041]** Alloy samples with metal additives other than iron were also prepared according to *different* embodiments.  $Gd_5Ge_2Si_2$  compounds alloyed or doped with Co, Cu, Ga, or Mn metal additives were prepared in the same manner as the  $Gd_5Ge_{1.9}Si_2Fe_{0.1}$ , i.e. by arc melting the appropriate elemental mixtures, using a water-cooled copper hearth in an argon atmosphere under ambient pressure. Approximately one atomic percent of the metal additive was added to the  $Gd_5Ge_2Si_2$  compound. The purity of the starting constituents was 99.9 wt. % and the chemical compositions of the alloy samples were as follows:  $Gd_5Ge_{1.9}Si_2Co_{0.1}$ ,  $Gd_5Ge_{1.9}Si_2Cu_{0.1}$ ,  $Gd_5Ge_{1.9}Si_2Ga_{0.1}$ , and  $Gd_5Ge_{1.9}Si_2Mn_{0.1}$ . As in the case of the  $Gd_5Ge_{1.9}Si_2Fe_{0.1}$  alloy of the first embodiment, each alloy was homogenized for one hour at 1300° C. in a vacuum prior to making magnetic measurements using a SQUID magnetometer.

**[0042]** Referring to FIGS. 2(a)-(d), which, respectively, depict backscattered SEM micrographs of the heat treated  $Gd_5Ge_2Si_2$  compound doped with cobalt, copper, gallium and manganese 14, 15, 16 and 17, the  $Gd_5Ge_2Si_2$  compounds doped with the metal additives have a microstructure consisting of a brighter dominant matrix phase and a darker minor phase delineating the grain boundaries of the matrix phase unlike the undoped single phase  $Gd_5Ge_2Si_2$  compound 10 (FIG. 1).

**[0043]** Referring to FIGS. 5(a)-(d), which, respectively, depict sets of hysteresis loops 18, 19, 20 and 21 showing the variation of magnetization, M, as a function of applied magnetic field, H, for the  $Gd_5Ge_{1.9}Si_2Mn_{0.1}$  17,  $Gd_5Ge_{1.9}Si_2Ga_{0.1}$  16,  $Gd_5Ge_{1.9}Si_2Cu_{0.1}$  15, and  $Gd_5Ge_{1.9}Si_2Co_{0.1}$  14 compounds, these Figures qualitatively illustrate the corresponding hysteresis losses of the compounds with the metal additives in the 260-320 K temperature range. The magnetization versus field loops 18, 19, 20 and 21 for these alloys were obtained in the same way as for the  $Gd_5Ge_{1.9}Si_2Fe_{0.1}$  compound by isothermally measuring the magnetization as a function of applied field from 260 to 320 K at each 10 K interval. For each loop, the field was cycled from zero to 5 T and back to zero.

**[0044]** The hysteretic loss values summarized in the Table 22, shown in FIG. 9, provide a quantitative comparison for the metal additive-free alloy and alloys with the metal additives. From this comparison, it can be clearly seen that the addition of about one atom percent of silicide-forming metals to the  $Gd_5Ge_2Si_2$  alloy resulted in a reduction of the hysteresis losses by more than 90 percent compared to the alloy without any metal additives and, for the metal additives Mn, Cu, and Ga, the hysteresis losses were nearly or completely eliminated, that is the reduction was nearly 100 percent.

**[0045]** Additional insight concerning the effect of the silicide forming metals on the magnetocaloric response of the  $Gd_5Ge_2Si_2$  compound in the 270-320 K temperature range

can be obtained by examination of the magnetization versus field loops shown in FIGS. 3, 4 and 5(a)-5(d). For the undoped  $Gd_5Ge_2Si_2$  alloy 10 containing no metal additive (FIG. 3), the magnetization versus field loops 12 show a distinct magnetic transition with increasing field for all temperatures between 270-290 K. Note that this transition occurs at higher field values with increasing temperature. Gschneidner and Pecharsky and their coworkers at Ames Laboratory hypothesized that this transition is the result of a field-induced first order magnetic transition from the paramagnetic monoclinic phase to the ferromagnetic orthorhombic phase. The magnetization versus field loops 12 appear to show that this field-induced transition is reversible upon decreasing field. However, the field at which the reversed transition occurs is smaller than the field required for inducing the original transition. Below 270 K, the alloy is ferromagnetic and above 295 K the material is paramagnetic.

**[0046]** By contrast, the magnetization versus field loops 13 of the alloy 11 containing iron (FIG. 4) do not show any field-induced magnetic transition in the 260-320 K temperature range for fields up to 5 T. In this temperature range, in fact, the magnetic data show a gradual shift from a ferromagnetic behavior to superparamagnetic behavior at about 300 K up to 320 K; above 320 K the material becomes paramagnetic. As already discussed, the compound without any metal additive becomes paramagnetic above 290 K. In addition, the M versus H data for the quaternary alloys do not indicate the presence of any magnetic transition for  $T < 260$  K. Therefore, the behavior of the alloys with and without the metal additives strongly suggests that one of the main effects of either iron or the other silicide-forming metal additives is to suppress the monoclinic-to-orthorhombic field-induced phase transition in the 270-320 K range, resulting in much smaller hysteresis losses.

**[0047]** Referring to FIGS. 6 and 7, which, respectively, depict graphs 23 and 24 of computed magnetic entropy change,  $\Delta S_m$ , versus temperature of the heat treated  $Gd_5Ge_2Si_2$  compound and the heat treated  $Gd_5Ge_{1.9}Si_2Fe_{0.1}$  alloy, variation of the magnetic entropy change,  $\Delta S_m$ , with temperature for the metal additive-free alloy and alloy with iron additive is observed. Also, variation of the magnetic entropy change for the alloys with other metal additives is also observed as shown in FIG. 8, which depicts a graph 25 of computed magnetic entropy change,  $\Delta S_m$ , versus temperature of the different heat treated  $Gd_5Ge_{1.9}Si_2Co_{0.1}$  14,  $Gd_5Ge_{1.9}Si_2Mn_{0.1}$  17,  $Gd_5Ge_{1.9}Si_2Cu_{0.1}$  15, and  $Gd_5Ge_{1.9}Si_2Ga_{0.1}$  16 alloys of the embodiments. These data were computed from the isothermal M vs. H data of the alloys using the integrated form of the Maxwell relation and a numerical integration routine.

**[0048]** The data presented in FIGS. 6-8 clearly show the following significant differences regarding the magnetic entropy change,  $\Delta S_m$ , as a function of temperature for the alloy without and the alloys with the metal additives. First, for the alloy without any metal additives, the value of the  $\Delta S_m$  peak, integrated over an applied field,  $\Delta H = 5$  T, is about a factor of 3 higher than of the alloys with the metal additives (20 J/kg-K vs. 7 J/kg-K). Secondly, the  $\Delta S_m$  peaks for the metal additive-containing alloys are considerably broader (FIGS. 7 and 8). Thirdly, the peak of  $\Delta S_m$  occurs at about 305 K for these latter alloys, whereas in the alloy without the metal additives the  $\Delta S_m$  peak occurs at about 275 K.

**[0049]** From the data presented in FIGS. 6-8, the refrigeration capacity value was computed for each alloy. The refrig-