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Magnetic and magnetocaloric properties of $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La)

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Phase compositions and crystal structures of $Gd_6X_2Si_3$ (X = Ni, Co,) and $Ln_6Co_2Si_3$ (Ln = Pr, La) have been studied. The magnetic properties of $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La) have been evaluated from magnetization measurements performed by a superconducting quantum interference device magnetometer in a temperature interval of 5–400 K, and at magnetic fields up to 5 T. The crystal structures of $Gd_6X_2Si_3$ (X = Co, Ni) and $Ln_6Co_2Si_3$ (Ln = Pr, La) were found to be hexagonal at 300 K. The Curie temperature (T_C), effective and magnetic moment of the compounds (at 5 K) have been determined for $Gd_6X_2Si_3$ (X = Ni, Co), and $Ln_6Co_2Si_3$ (Ln = Pr, La). T_C was found to depend on composition, and reaches maximum value of about 300 K for the $Gd_6X_2Si_3$ system. The magnetocaloric effect (magnetic entropy changes and relative cooling power (RCP) was found to depend on X and Ln, and the maximum RCP values were found to be larger than 500 J/kg near room temperature for the $Gd_6Ni_2Si_3$ and $Gd_6Co_2Si_3$ compounds. This value of RCP is comparable to the prototype magnetic refrigeration material, Gd. © *2011 American Institute of Physics*. [doi:10.1063/1.3544509]

The magnetocaloric effect (MCE) results from changes in the magnetic order of materials and, therefore, the most appreciable MCE can be expected in the vicinity of magnetic phase transitions induced by temperature and/or magnetic fields. The value of the MCE depends on the difference in the magnetic state before and after temperature or field induced phase transitions (PT). The largest MCE can therefore be expected at first-order transitions (FOT) where jumplike changes in magnetization are observed.[1] The MCE associated with a FOT is also subject to hysteresis effects. The MCE related to a second order transition (SOT) possesses significantly less hysteresis. The search and study the compounds that produce low hysteresis losses is important from an application prospective. The $R_6Co_2Si_3$ compounds attract attention due to their high concentration of magnetic ions per formula unit and, therefore, to their potential for extreme changes in magnetic and other related properties that are linked to PT. Since they can be made to magnetically order near 300 K the compounds can be considered as potentially new magnetocaloric and multifunctional systems. The magnetic transition in Gd_6Co_2Si should be close to room temperature (RT) and is reversible in both temperature and field with a large relative cooling power (RCP = 430 J/kg).[2] The existence of $R_6Co_2Si_3$ (R = La, Ce, Pr, Nd) compounds with the hexagonal $Ce_6Ni_2Si_3$ type crystal structure were reported in ternary phase diagram in Ref. 3 It has been shown in Refs. 4 and 5 that stoichiometric R_6X_2Si does not exist and, therefore the $R_6X_{5/3}Si_3$ off-stoichiometric composition should be considered as a single phase. On the other hand, single phase polycrystalline as well as single crystals of the ternary silicides of $R_6X_2Si_3$ with stoichiometric composition have been reported in Refs. 2, 6, and 7.

In this work, the phase compositions at RT magnetic properties, and MCE parameter such as magnetic entropy changes in vicinity of TC and RCP of $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La) compounds have been studied.

Approximately 5 g polycrystalline $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La) samples were fabricated by conventional arc melting in an Ar atmosphere using high purity elements followed by annealing in vacuum ($\approx 10^{-4}$ Torr) for 15 days at 800 °C. The phase purity and crystal structures were determined by room-temperature powder x-ray diffraction (XRD) using Cu K_α radiation. Thermomagnetic curves $M(T,H)$ were measured using a superconducting quantum interference device (SQUID) magnetometer (by Quantum Design, USA) in the temperature interval 5–400 K and in magnetic fields up to 5 T. All measurements were carried out during heating after the samples were cooled from 400 to 5 K in zero magnetic field (ZFC). The transition temperatures were determined from the local maxima of dM/dT of the ZFC $M(T)$ curves. The effective paramagnetic moments (μ_{eff}) were calculated from the linear parts of inverse susceptibility, χ^{-1} (T), curves in H=5T. The magnetic entropy changes $\Delta S_M(T, H)$ were calculated from isothermal magnetization curves $M(H, T)$ using the Maxwell relation (1). The RCP was estimated by multiplying ΔS_M peak value by δT_{FWHM} determined from the full width at half maximum (FWHM) of the ΔS_M (H,T) curves using Eq. (2) (Refs. 8 and 9) below.

$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH, \tag{1}$$

$$\text{RCP} = -\Delta S_M^{\text{peak}} \times \delta T_{\text{FWHM}}. \tag{2}$$

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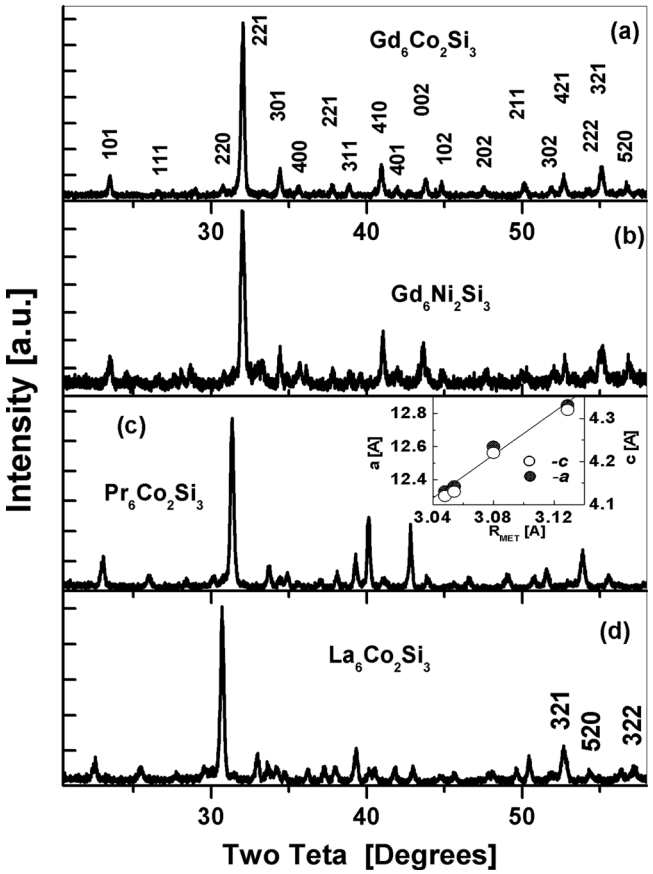

FIG. 1. (a)–(d) Room temperature XRD patterns for $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La); Inset: *c* and *a* cell parameters of the hexagonal structure of $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La) compounds depend on metallic radii $R_{MET} = (R_{Ln} + R_X)$.

The room temperature XRD patterns for $Gd_6X_2Si_3$ (X = Ni, Co,), $Ln_6Co_2Si_3$ (Ln = Pr, La), are shown in Fig.1(a)–1(d). A $Ce_6Ni_2Si_3$–type hexagonal structure was detected for the compounds. The samples contain of about 5–10% of phase impurities. The lattice parameters, *a* and *c*, of $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La) systems were found to increase linearly with increasing metallic radii (R_{MET}) (Ref. 10) of elemental components from ($a = 3.05$ Å, $c = 12.3$ Å) to ($a = 3.13$ Å, $c = 12.8$Å) for $Gd_6Ni_2Si_3$ and $La_6Co_2Si_3$, respectively [see inset on Fig. 1(d)]. The c/a ratio remains constant, (c/a ≈ 4), for all compounds.

All compounds exhibit a ferromagnetic type of $M(H)$ behavior at 5 K (see Fig. 2). The $M(H)$ curves can be described, starting from a certain field, as $M(H) = M_0 + \chi_H H$, where the constants, M_0 and χ_H, are the magnetization and the magnetic susceptibility, respectively. The shape of the $M(H)$ curves of collinear ferromagnetic compounds at low magnetic field are determined by domain structure and magnetocrystalline anisotropy. In this case the constant M_0 is the magnetization of the single domain ferromagnetic compound with zero anisotropy at H = 0. The values of magnetic moment of formula unit (m_0) calculated using M_0 [obtained from the $M(H)$ curves shown in Fig. 2] are collected in Table I. The M(T) curves at H = 0.01T, along with χ(T)-1 at 5T are shown in Fig. 3. $M(T)$ of all the compounds are characterized by sharp,

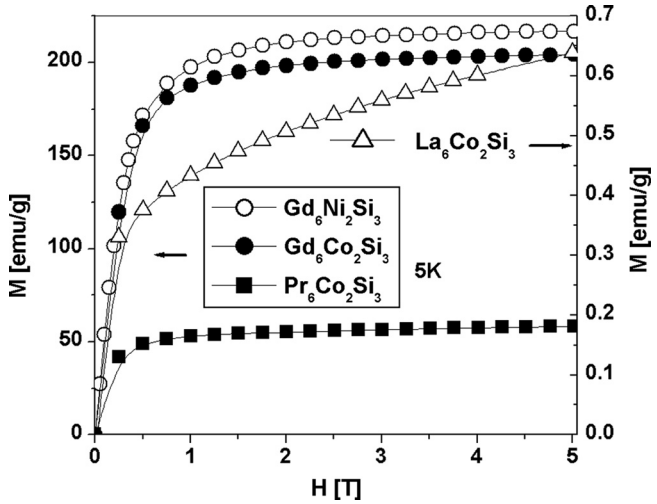

FIG. 2. Magnetization curves $M(H)$ at 5 K for $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La).

ferromagnetic type changes in the magnetization at T_C. $La_6Co_2Si_3$ shows a non-Curie–Weis type of magnetization above T_C, reflecting the itinerant character of 3d magnetism in these compounds, and characterized by low $T_C = 7$ K and $m_0 = 0.04$ μ_B per Co atom (see Table I). Therefore *d–d* exchange interaction is not significant in $Ln_6X_2Si_3$ compounds. The TC increases rapidly from 50 to 298 K (319 K) for $Pr_6Co_2Si_3$ and $Gd_6Co_2Si_3$ ($Gd_6Ni_2Si_3$).

The experimental values of μ_{eff} and the paramagnetic Curie temperatures, Θ_P, calculated from the linear part of $\chi^{-1}(T)$ are shown in Table I. The small difference in Θ_P and T_C observed for $Gd_6X_2Si_3$ (X = Ni, Co) is consistent with the ferromagnetic character of the magnetic ordering in the compounds. As can be seen from the Table I, m_0 of $Gd_6X_2Si_3$ is similar to that of Gd^{+3} (42 μ_B/f.u.). Thus, one can suggest a collinear ferromagnetic structure in $Gd_6X_2Si_3$ (X = Ni, Co), at least at low temperature region. The observed experimental values of $\mu_{eff} \approx 9$ μ_B/Gd (see Table I) are larger than the calculated value for Gd^{+3} (7.96 μ_B/Gd). This can be a result of short-range magnetic correlations above T_C, or from undetected magnetic impurities. In the case of $Pr_6Co_2Si_3$, the values of $\mu_{eff} \approx 3.8$ μ_B/Pr is relativity close to the calculated value for Pr^{+3} (3.6 μ_B/Pr) while m_0 and Θ_P are considerably smaller than $m_0 = 19.2$ μ_B/(f.u.) expected for Pr^{+3} and the observed T_C, respectively. Such behavior can be considered as evidence for the presence of antiferromagnetic interactions in $Pr_6Co_2Si_3$, resulting in a noncollinear or ferrimagnetic type of magnetic structure. This conclusion is in agreement with the results reported in Ref. 11. The sharp increase in ZFC magnetization of the $Pr_6Co_2Si_3$ compound observed before T_C (see Fig. 3) is most likely related to large magnetocrystalline

TABLE I. Some magnetic and magnetocaloric parameters of $Gd_6X_2Si_3$ (X=Ni, Co) and $Ln_6Co_2Si_3$ (Ln=Pr, La) compounds.

Compounds	T_C (K)	Θ_P(K)	m_0 (μ_B/f.u.)	μ_{eff} (μ_B/f.u.)	ΔS_M (J/kgK)	RCP J/Kg
$Gd_6Ni_2Si_3$	319	309	43.1	22	4.2	521
$Gd_6Co_2Si_3$	298	295	40.4	21.3	5.3	519
$Pr_6Co_2Si_3$	50	34	10	9.3	6.1	205
$La_6Ni_2Si_3$	7	Not C.-W.	0.08	–	0.1	

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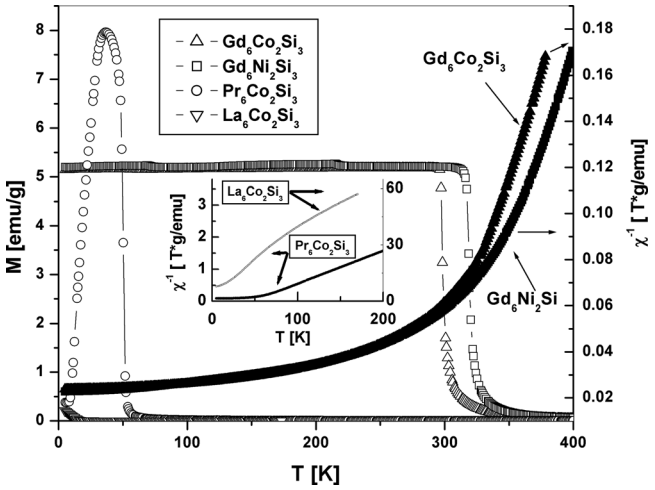

FIG. 3. $M(T)$ curves at $H = 0.01$ T for $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr, La); $\chi^{-1}(T)$ at 5 T for $Gd_6X_2Si_3$ (X = Ni, Co) and $Ln_6Co_2Si_3$ (Ln = Pr inset, left panel, Ln = La, inset, right panel).

anisotropy that originates from the orbital component of the Pr total magnetic moment (which is equal zero in the case of Gd and La metals). Taking into account that $T_C = 294$ K for Gd is similar to that observed for $Gd_6X_2Si_3$ (X = Ni, Co), and the low T_C and m_o of $La_6Ni_2Si_3$ (see Table I), one can conclude that *f–f* exchange interaction is mostly responsible for the magnetic behavior of $Ln_6X_2Si_3$ compounds. The observed difference in T_C of $Gd_6Ni_2Si_3$ and $Gd_6Co_2Si_3$ compounds is most likely due to a difference in the conduction electron concentration and/or differences in crystal cell volume.

In order to evaluate the MCE parameters the isothermal measurements of magnetization in vicinity of the T_C have been performed. The M(H) curves for different ΔH are shown in Fig. 4 for $Gd_6Ni_2Si_3$. The $Gd_6Co_2Si_3$ and $Pr_6Co_2Si_3$ demonstrate a similar behavior. The maxima of ΔS_M and RCP for $\Delta H = 5$ T calculated using Eqs. (1) and (2) are collected in Table I. The compounds are characterized by a broad maximum of ΔS_M in vicinity of T_C. Such behavior is in agreement with other reports (see Refs. 2, 4, and 12) and results in the large RCP for Gd compounds (see Table I). The maximum ΔS_M for $\Delta H = 5$ T was found to be ≈ 4.2 and 5.3 J kg^{-1} K^{-1} for $Gd_6Co_2Si_3$ and $Gd_6Ni_2Si_3$, respectively. The ΔS_M increases almost linearly with ΔH and does not saturate for $\Delta H = 5$ T. The RCP in the vicinity of T_C, was found to be maximum for $Gd_6X_2Si_3 \approx 520$ J/kg $\Delta H = 5$ T. It is interesting to note here that the maximum of ΔS_M slightly increase in value while RCP decreases more than two times for $Pr_6Ni_2Si_3$ compared to that for $Gd_6X_2Si_3$ (see Table I). Such behavior is most likely related to the difference in T_C and in magnetic structures of these compounds.

The results of the presented studies of $Gd_6X_2Si_3$ (X = Co, Ni) and $Ln_6Co_2Si_3$ (Ln = Pr, La) have been shown that (i) the crystal cell parameters are a linear function of the metallic radii of the elemental components of the compounds, and c/a ratio remains nearly constant ($c/a \approx 4$) across all of the compounds under consideration; (ii) *f–f* exchange interaction is the major interaction that determines the magnetic behavior of the systems; (iii) the magnetic structures of $Pr_6Co_2S_3$ and $Gd_6X_2Si_3$ (X = Co, Ni) are different; and (iv) the large RCP

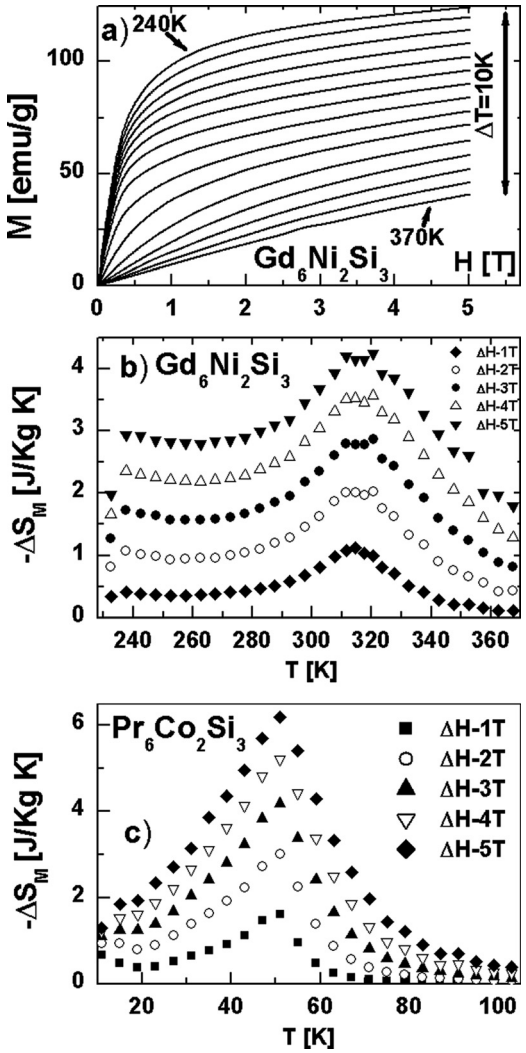

FIG. 4. (a) Magnetization isotherms of $Gd_6Ni_2Si_3$ in the vicinity of T_C and (b) $\Delta S_M(T)$ calculated from the data in (a) for different applied field changes.

(≈ 520 J/kg) values have been observed for $Gd_6X_2Si_3$ (X = Co, Ni). These values are comparable to that of Gd, the original prototype material for magnetic refrigeration applications.

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