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Magnetic and magnetocaloric properties of Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La)

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Phase compositions and crystal structures of Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La) have been studied. The magnetic properties of Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (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 Gd₆X₂Si₃ (X = Co, Ni) and Ln₆Co₂Si₃ (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 Gd₆X₂Si₃ (X = Ni, Co), and Ln₆Co₂Si₃ (Ln = Pr, La). T_C was found to depend on composition, and reaches maximum value of about 300 K for the Gd₆X₂Si₃ 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 Gd₆Ni₂Si₃ and Gd₆Co₂Si₃ compounds. This value of RCP is comparable to the prototype magnetic refrigeration material, Gd.

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. 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 R₆Co₂Si₃ 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 Gd₆Co₂Si₃ 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 R₆Co₂Si₃ (R = La, Ce, Pr, Nd) compounds with the hexagonal Ce₆Ni₂Si₃ type crystal structure were reported in ternary phase diagram in Ref. 3. It has been shown in Refs. 4 and 5 that stoichiometric R₆X₂Si₃ does not exist and, therefore, the R₆X₃/3Si₃ 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 R₆X₂Si₃ 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 Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La) compounds have been studied. Approximately 5 g polycrystalline Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La) samples were fabricated by conventional arc melting in an Ar atmosphere using high purity elements followed by annealing in vacuum (≈10⁻³ 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 Kα 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, 1/μ_eff(T), curves in H=5T. The magnetic entropy changes ΔS_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.

\[
ΔS_M(T,H) = \int_0^H \left( \frac{∂M}{∂T} \right)_H dH, \quad (1)
\]

\[
\text{RCP} = -ΔS^\text{peak}_M \times δT_FWHM. \quad (2)
\]

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La₆Co₂Si₃, respectively [see inset on Fig. 1(d)]. The c/a ratio calculated using $\frac{c}{a} = \frac{R_{TM}}{R_L}$ found to increase linearly with increasing metallic radii $R$ (Co, Ln). Gd₆Co₂Si₃ (Ln = Ce₆Ni₂Si₃–type hexagonal structure was detected for the shape of the structure and magnetocrystalline anisotropy. In this case pounds at low magnetic field are determined by 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 $\gamma(T)$ of all the compounds are characterized by sharp, ferromagnetic type changes in the magnetization at $T_C$. Ln₆Co₂Si₃ shows a non-Curie–Weiss 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 $m_0 = 0.04 \mu_B$ per Co atom (see Table I). Therefore $d-d$ exchange interaction is not significant in Ln₆X₂Si₃ compounds. The TC increases rapidly from 50 to 298 K (319 K) for Pr₆Co₂Si₃ and Gd₆Co₂Si₃ (Gd₆Ni₂Si₃).

The experimental values of $\mu_{eff}$ and the paramagnetic Curie temperatures, $\Theta_P$, calculated from the linear part of $\gamma^{-1}(T)$ are shown in Table I. The small difference in $\Theta_P$ and $T_C$ observed for Gd₆X₂Si₃ (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 Gd₆X₂Si₃ is similar to that of Gd₃⁺ (42 $\mu_B$/f.u.). Thus, one can suggest a colinear ferromagnetic structure in Gd₆X₂Si₃ (X = Ni, Co), at least at low temperature region. The observed experimental values of $\mu_{eff}$ ≈ 9 $\mu_B$/Gd (see Table I) are larger than the calculated value for Gd₃⁺ (7.96 $\mu_B$/Gd). This can be a result of short-range magnetic correlations above $T_C$ or from undetected magnetic impurities. In the case of Pr₆Co₂Si₃, the values of $\mu_{eff}$ ≈ 3.8 $\mu_B$/Pr is relatively close to the calculated value for Pr₃⁺ (3.6 $\mu_B$/Pr) while $m_0$ and $\Theta_P$ are considerably smaller than $m_0 = 19.2 \mu_B$/f.u. expected for Pr₃⁺ and the observed $T_C$, respectively. Such behavior can be considered as evidence for the presence of antiferromagnetic interactions in Pr₆Co₂Si₃, 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 Pr₆Co₂Si₃ compound observed before $T_C$ (see Fig. 3) is most likely related to large magnetocrystalline anisotropy.

![FIG. 1. (a)–(d) Room temperature XRD patterns for Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La); Inset: c and a cell parameters of the hexagonal structure of Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La) compounds depend on metallic radii $R_{MET} = (R_L + R_X)$.](image)

![FIG. 2. Magnetization curves $M(H)$ at 5 K for Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La).](image)

### Table I. Some magnetic and magnetocaloric parameters of Gd₆X₂Si₃ (X = Ni, Co) and Ln₆Co₂Si₃ (Ln = Pr, La) compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_C$ (K)</th>
<th>$\Theta_P$ (K)</th>
<th>$m_0$ (\mu_B/f.u.)</th>
<th>$\mu_{eff}$ (\mu_B/f.u.)</th>
<th>$\Delta S_M$ (J/KgK)</th>
<th>RCP J/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd₆Ni₂Si₃</td>
<td>319</td>
<td>309</td>
<td>43.1</td>
<td>22</td>
<td>4.2</td>
<td>521</td>
</tr>
<tr>
<td>Gd₆Co₂Si₃</td>
<td>298</td>
<td>295</td>
<td>40.4</td>
<td>21.3</td>
<td>5.3</td>
<td>519</td>
</tr>
<tr>
<td>Pr₆Co₂Si₃</td>
<td>50</td>
<td>34</td>
<td>10</td>
<td>9.3</td>
<td>6.3</td>
<td>205</td>
</tr>
<tr>
<td>Ln₆Ni₂Si₃</td>
<td>7</td>
<td>Not C.-W.</td>
<td>0.08</td>
<td>-</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>
Such behavior is most likely related to the difference in TC to be maximum for Ga6X2Si3 compared to that for Pr6Ni2Si3 (see Table I). The increase in value while RCP decreases more than two times for Pr6Ni2Si3 demonstrate a similar behavior. The maxima of D in agreement with other reports (see Refs. 2, 4, and 12) and in magnetic structures of these compounds.

The results of the presented studies of Ga6X2Si3 (X = Ni, Co) and Ln6Co2Si3 (Ln = Pr, La); χ(−1)(T) at T = 5 T for Ga6X2Si3 (X = Ni, Co) and Ln6Co2Si3 (Ln = Pr inset, left panel, Ln = La, inset, right panel).

In order to evaluate the MCE parameters the isothermal measurements of magnetization in vicinity of the TC have been performed. The M(H) curves for different field are shown in Fig. 4 for Ga6Ni2Si3. The Ga6Co2Si3 and Pr6Co2Si3 demonstrate a similar behavior. The maxima of ΔM and RCP for ΔH = 5 T calculated using Eqs. (1) and (2) are collected in Table I. The compounds are characterized by a broad maximum of ΔM in vicinity of TC. Such behavior is in agreement with other reports (see Refs. 2, 4, and 12) and results in the large RCP for Ga6Co compounds (see Table I). The maximum ΔM for ΔH = 5 T was found to be ≈ 4.2 and 5.3 J kg−1 K−1 for Ga6Co2Si3 and Ga6Ni2Si3, respectively. The ΔM increases almost linearly with ΔH and does not saturate for ΔH = 5 T. The RCP in the vicinity of TC, was found to be maximum for Ga6X2Si3 ≈ 520 J/kg ΔH = 5 T. It is interesting to note here that the maximum of ΔM slightly increase in value while RCP decreases more than two times for Pr6Ni2Si3 compared to that for Ga6X2Si3 (see Table I). Such behavior is most likely related to the difference in TC and in magnetic structures of these compounds.

The results of the presented studies of Ga6X2Si3 (X = Co, Ni) and Ln6Co2Si3 (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 ≈ 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 Pr6Co2Si3 and Ga6X2Si3 (X = Co, Ni) are different; and (iv) the large RCP (≈ 520 J/kg) values have been observed for Ga6X2Si3 (X = Co, Ni). These values are comparable to that of Gd, the original prototype material for magnetic refrigeration applications.

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FIG. 3. M(ΔT) curves at H = 0.01 T for Ga6X2Si3 (X = Ni, Co) and Ln6Co2Si3 (Ln = Pr, La); χ(−1)(T) at T = 5 T for Ga6X2Si3 (X = Ni, Co) and Ln6Co2Si3 (Ln = Pr inset, left panel, Ln = La, inset, right panel).

FIG. 4. (a) Magnetization isotherms of Ga6Ni2Si3 in the vicinity of TC and (b) ΔM(ΔH) calculated from the data in (a) for different applied field changes.

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