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# Oscillations in magnetocaloric effect and magnetic properties of $RE_2Al_3Si_2$ (for RE = Dy, Ho and Er) and REAlSi (for RE = Ce and Pr)

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**Abstract**

We present the magnetic and thermal properties of a series of compounds $RE_2Al_3Si_2$ for RE = Dy, Ho, Er, and REAlSi for RE = Pr, Ce. The 2–3–2 family crystallizes with themonoclinic $Y_2Al_3Si_2$-type structure while the 1–1–1 family crystallizes in the body-centered tetragonal α-$ThSi_2$-type structure. The measurements were done on single crystals, grown using high-temperature flux technique and molten Al as a solvent . Susceptibility and heat capacity data were taken from 1.8 to 200 K, from the heat capacity data, the isothermal magnetic entropy change was obtained. Our results indicate signal oscillations in magnetocaloric properties for those compounds, in particular, $Dy_2Al_3Si_2$ that shows an anomaly that can be associated with a spin reorientation. Similar results are known for some Dy discilicides and dialluminades.
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## 1. Introduction

The properties of rare-earth intermetallic compounds were extensively revisited after the discovery of the giant magnetocaloric effect (GMCE) [1] in order to investigate their potential for refrigeration. The ordinary magnetocaloric effect (MCE), which is present in all magnetic materials, is observed as a change in temperature of a material under an applied magnetic field; on the other hand, the phenomenon is amplified almost two order of magnitude higher in materials with GMCE. Therefore, there has been an interest in understanding the reasons that would lead to GMCE; for instance, several reports proved the influence of crystalline field effects (CEF) and second-order contribution (magnetoelastic and quadrupolar), in particular the Laves Phases compounds, on the general behavior of the MCE [2–8].

The discovery of GMCE is also considered the starting point of a new era for magnetic refrigeration technology since it opened the possibility of finding economically viable materials to be used on an industrial scale, such as space-based applications and industrial cooling systems stations.

The search for new magnetic refrigerant materials has been on focus in the last few years. The focus is mostly on the ferromagnetic compounds which present maximum MCE near/at the ordering temperature. Moreover, the effort is also concentrated on the materials that present MCE near room temperature such as $Gd_5(Si_{1-x}Ge_x)_4$ [1], $MnFeP_{1-x}As_x$ [9] and MnAs [10]; however, other materials, such as $RE_2InGe_2$, were also investigated as possible candidates to be used as a refrigerant material for low temperatures. Other compounds such as $REAl_2$ and pseudo binary $(RE,Er)Al_2$ with concentration of $Er \geqslant 0.75$ [11] were proven to be good refrigerant materials as well as

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useful compounds to explore and improve theoretical approaches.

The interest in the binary rare-earth dialluminades [12] and sillicides [13–15] compounds has grown in the past few years since they are suitable for technologic applications such as electronic devices. Recently, some of us presented a new series, $RE_2Al_3Si_2$, of compounds in a report on the crystal structure [16] and on some preliminary transport properties; however, there are no reports on their magnetocaloric and magnetic properties, as far as we are aware. Theoretical description is in progress and will be published somewhere else.

In the present work, we present the magnetic and thermal properties of the ternary $RE_2Al_3Si_2$ for RE = Dy, Ho and Er , and for REAlSi for RE = Pr and Ce. The heat capacity of 0 and 5 T for the temperature range from 1.8 to 200 K were taken using a quantum design PPMS. The susceptibility data were taken in SQUID magnetometer for a low temperature, from 1.8 to 50 K. We calculated the isothermal magnetic entropy change ($\Delta S_{mag}$), using the Maxwell's thermodynamic relations, $C_{p,B} = T(\partial S/\partial T)_{p,B}$ and taking the difference between the entropy without an applied field and the entropy with an applied field:

$$-\Delta S_M(T, B_0) = S(T, B_0 = 0) - S(T, B_0) = S_M(T, B_0 = 0) - S_M(T, B_0).$$

The $\Delta S_{mag}$ curve as a function of the temperature presented anomalous behavior.

## 2. Sample preparation

The series $RE_2Al_3Si_2$ for RE = Ce goes $RAl_xSi_{2-x}$, ternary derivatives of the body-centered $\alpha$-$ThSi_2$-type structure, while for RE = Dy, Ho, Er and Tm the compound crystallizes in the C-centered monoclinic $Y_2Al_3Si_2$-type structure. The samples were grown using high-temperature flux technique using molten Al as a solvent. Rare-earth metals with >99.9% purity from Ames Laboratory were used as received, while Al (shot) and Si (lump), both with purity greater than 99.999% were obtained from Alfa-Aesar. X-ray powder diffraction patterns were taken on a Scintag XDS 2000 with monochromated Cu K$\alpha$ radiation, results indicated the sample were single phase. Our studies carried out from RE = La to Gd which invariably yields $REAl_xSi_{2-x}$ with the $\alpha$-$ThSi_2$ structure. For the rare earths heavier than Gd, from Tb to Lu, the $Y_2Al_3Si_2$ structure is favored. The last lanthanide element, Lu, though, under the same conditions can also form LuAlSi with the YAlGe type, a deviation from the general trends that is most certainly due to very small ionic size and/or completely filled f-shell. Eu and Yb are certainly exceptions from the two subgroups due to their tendency to be in divalent oxidation states, a result of the stabilization of half filled and completely filled f-shells for $Eu^{2+}$ and $Yb^{2+}$, respectively. Thus, independent of the differences in the $Eu^{2+}$ and $Yb^{2+}$ ionic radii, the corresponding Eu–Al–Si and Yb–Al–Si reactions at these specific conditions (above) yield $RAl_2Si_2$ (R = Eu, Yb) with the trigonal $CaAl_2Si_2$ type. Further details on the phase relations in the systems can be found elsewhere [16].

## 3. Results

Fig. 1 shows the susceptibility data as a function of the temperature for CeAlSi (a), PrAlSi (b), $Ho_2Al_3Si_2$ (c), $Dy_2Al_3Si_2$ (d), $Er_2Al_3Si_2$ (e). In the $Ho_2Al_3Si_2$, two clear peaks in the susceptibility were observed, indicating two successive magnetic transitions or spin reorientation. The peak in lower temperatures can be associated to spin reorientation, while the other one at higher temperature is associated with the ordered/disordered transition. From the inverse of the susceptibility data, we can extract the effective magnetic moment and the critical temperatures, $\mu_{eff} = 9.68\,\mu_B$ ($T_N = 4.2$ K), $\mu_{eff} = 2.5\,\mu_B$ ($T_C < 4.2$ K), $\mu_{eff} = 10.66\,\mu_B$ ($T_C = 11.8$ K), $\mu_{eff} = 10.4\,\mu_B$ ($T_N = 7.8$ K),

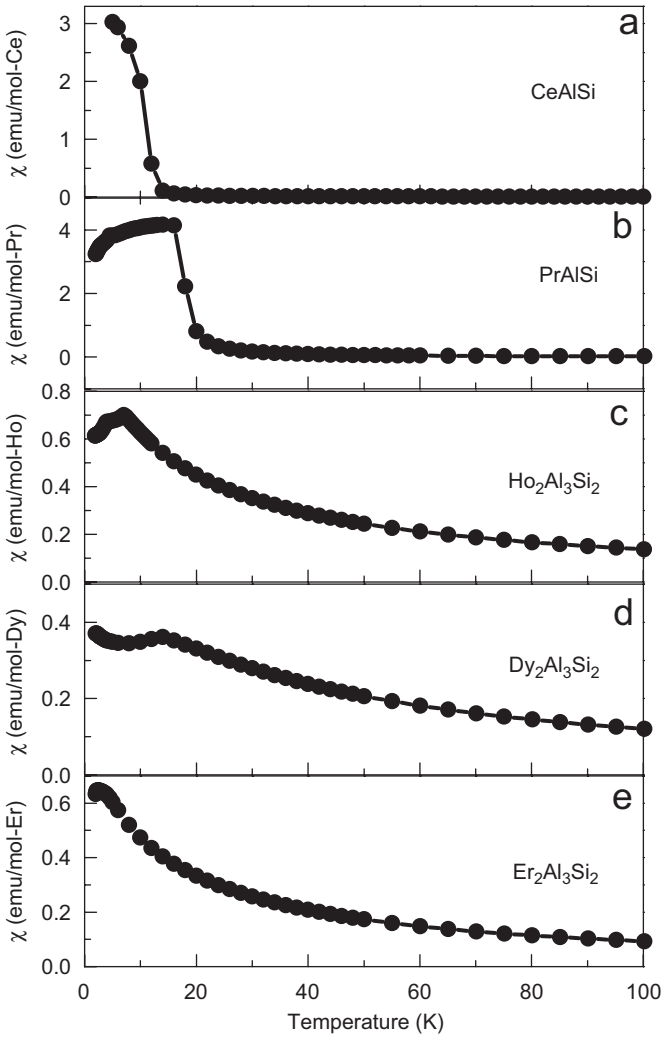


Fig. 1. The susceptibility as a function of as a function of the temperature for CeAlSi, PrAlSi, $Ho_2Al_3Si_2$, $Dy_2Al_3Si_2$ and $Er_2Al_3Si_2$.