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The influence of spontaneous and field-induced spin reorientation transitions on the magnetocaloric properties of HoZn and ErZn

V. S. R. de Sousa, P. J. von Ranke, and F. C. G. Gandra

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We report a theoretical investigation on the magnetocaloric properties of the cubic CsCl-type HoZn and ErZn compounds. Several anomalies in the magnetocaloric quantities, $\Delta S_T$ and $\Delta T_S$, are observed due to spontaneous and/or field-induced spin reorientation transitions in these compounds. In HoZn, a discontinuity in the isothermal entropy change and in the adiabatic temperature change around $T_1 = 23$ K is ascribed to the spontaneous reorientation transition. Under a magnetic field variation from 0 up to 2 T in the $\langle110\rangle$ and $\langle100\rangle$ directions, an almost table-like behavior in $\Delta S_T$ is predicted between $T_1$ and $T_{SR1}$. The peak around the ferromagnetic–paramagnetic transition temperature in the magnetocaloric quantities shows a dependence on the direction of the applied field. For $\mu_0 H = 2$ T, it reaches 11.9 J/kg K (magnetic field along the $\langle111\rangle$ direction) and 7.9 J/kg K (magnetic field in the $\langle100\rangle$ direction). In ErZn there is also a dependence of $\Delta S_T$ and $\Delta T_S$ on field direction. From the analysis of the spin reorientations in both compounds we have built spin reorientation diagrams that summarize their temperature and field dependence. Our theoretical approach is based on a model Hamiltonian that includes exchange, crystal field, and quadrupolar interactions. © 2011 American Institute of Physics. [doi:10.1063/1.3554725]

I. INTRODUCTION

Research on the magnetocaloric effect (MCE), which is the thermal response of magnetic materials to a magnetic field, have intensively grown in the past thirteen years since the discovery of a giant magnetocaloric effect (GMCE) in Gd$_5$Si$_2$Ge$_2$ by Pecharsky and Gschneidner. The GMCE is the discovery of a giant magnetocaloric effect (GMCE) in rare-earth-based intermetallic compounds can induce a secondary peak in the MCE quantities with the same sign as the peak around the FM–PM transition temperature, and these two successive transitions induce high refrigerant capacities in these compounds.

The isotope GMCE observed as a function of the magnetic field and temperature.

As recently reported, the presence of SR transitions in rare-earth-based intermetallic compounds can induce a secondary peak in the MCE quantities with the same sign as the peak around the FM–PM transition temperature, and these two successive transitions induce high refrigerant capacities in these compounds.

The equiatomic RZn intermetallic compounds crystallize in the cubic CsCl-type structure. In this series, compounds formed with light lanthanides are antiferromagnets, whereas those formed with heavy lanthanides are ferromagnets whose Curie temperatures ($T_C$'s) lie between 269 and 17 K. Some magnetic, calorimetric, and magnetoelastic properties of the RZn compounds are reported in the literature, but few works have explored the MCE in this series. The aim of this work is to investigate the magnetocaloric properties of HoZn and ErZn. HoZn presents a first-order spontaneous reorientation transition (SRT) and its magnetization discontinuously rotates from the $\langle110\rangle$ direction toward the $\langle111\rangle$ one, as temperature increases at $T_1 = 23$ K. ErZn exhibit large magnetoelastic effects. To correctly describe the main characteristics of these two compounds quadrupolar interactions have to be considered, and consequently we can investigate how this second-order term affects the spin reorientations and the MCE in these intermetallics. The quadrupolar interaction consists of two contributions: a biquadratic coupling of the spins, and a coupling

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between the lattice and the 4f shell quadrupoles that gives rise to magnetoelastic effects.

In our theoretical investigation, a model Hamiltonian that takes into account the exchange, Zeeman, CF, biquadratic, and magnetoelastic interactions was considered. Our results for the specific heat and magnetization are in good agreement with the available experimental data. The magnetocaloric quantities, $\Delta S_T$ and $\Delta T_S$, were calculated considering the magnetic field applied along the three main cubic crystallographic directions $(100)$, $(110)$, and $(111)$.

II. THEORY

The compounds HoZn and ErZn are ferromagnets with $T_c$’s of 74 and 17 K and lattice constants of 3.547 and 3.532 Å, respectively. The cubic primitive structure, in which they crystallize, contains only one magnetic ion per unit cell, in a highly symmetric position. The description of their magnetic and magnetoelastic properties can be performed starting from the following single-ion Hamiltonian:

$$H = -g\mu_B(\mu_0 \mathbf{H} + \lambda \mathbf{M}) \cdot \mathbf{J} + H_{CF} + H_q + H_{me}. \quad (1)$$

The first term in Eq. (1) describes the action of an effective field, formed by an external and a molecular field, on the magnetic ion, $g$ is the Landé factor, $\mu_B$ the Bohr magneton, $\mu_0$ the vacuum permeability, $\mathbf{H}$ the applied magnetic field, $\lambda$ the exchange parameter, $\mathbf{M}$ the magnetization, and $\mathbf{J}$ the total angular momentum operator. $H_{CF}$ describes the crystal field anisotropy and it is determined by the rare-earth–site symmetry, which for the RZn compounds is $O_{h}$, and therefore it contains only the fourth- and sixth-order anisotropy terms. $H_{CF}$ can be written in the Lca–Leask–Wolf notation as:

$$H_{CF} = \frac{W}{F_4} \left[ O_{h}^0 + 5O_{h}^2 \right] + \frac{1 - |x|}{F_6} \left[ O_{h}^0 - 21O_{h}^2 \right]. \quad (2)$$

where $W$ is the energy scale and $x$ gives the ordination of the splitting of the degenerate Hund’s ground state, $O_{h}^n$ are Stevens’ operators, and $F_4$ and $F_6$ are dimensionless factors tabulated for each rare earth. The biquadratic Hamiltonian can be written in the mean-field approximation as follows:

$$H_q = -K_1 \left[ (O_{h}^0)^2 + 3(O_{h}^2)^2 \right] - 4K_2 \left[ (P_{xy})^2 (P_{xy}) + (P_{yz})^2 (P_{yz}) + (P_{xz})^2 (P_{xz}) \right], \quad (3)$$

where $K_1$ and $K_2$ are the biquadratic coupling parameters. $O_{h}^0$, $O_{h}^2$, and $P_{ij}$ ($ij = xy$, $yz$, $zx$) are second-order Stevens’s operators given by:

$$O_{h}^0 = 3J_z^2 - J(J + 1)$$
$$O_{h}^2 = J_z^2 - J_z$$
$$P_{ij} = \frac{1}{2} (J_i J_j + J_j J_i).$$

The magnetoelastic Hamiltonian is written as

$$H_{me} = -B_1 \left[ e_3 O_{h}^0 + \sqrt{3} e_2 O_{h}^2 \right] - B_2 \left[ e_{xy} (P_{xy}) + e_{yz} (P_{yz}) + e_{xz} (P_{xz}) \right], \quad (5)$$

where $B_1$ and $B_2$ are magnetoelastic parameters and the $e$’s are cubic symmetrized strain modes. By considering the elastic energy and after minimizing the free energy relative to the $e$’s, one obtains the following expression combining the biquadratic and magnetoelastic Hamiltonians:

$$H_{q-m} = -G_1 \left[ (O_{h}^0)^2 + 3(O_{h}^2)^2 \right] - G_2 \left[ (P_{xy})^2 (P_{xy}) + (P_{yz})^2 (P_{yz}) + (P_{xz})^2 (P_{xz}) \right] \quad (6)$$

and

$$G_1 = K_1 + \frac{B_1^2}{(C_{11} - C_{12})_0},$$
$$G_2 = 4K_2 + \frac{B_2^2}{(4C_{44})_0}. \quad (7)$$

The $C_{0}$’s are background elastic constants in the absence of magnetic interactions.

In the calculations the Hamiltonian (1) is diagonalized and its eigenvalues ($\langle \varepsilon_i \rangle$) and eigenvectors ($\langle \varepsilon_i \rangle$) are then obtained. The magnetization is calculated taking the mean value of the magnetic moment, i.e.,

$$M_k = \langle g\mu_B \sum_i \langle \varepsilon_i \rangle \rho_k | \varepsilon_i \rangle e^{-\varepsilon_i / k_BT} \rangle \sum_j \langle \varepsilon_j \rangle e^{-\varepsilon_j / k_BT} \rangle, \quad (8)$$

where $k_B$ is the Boltzmann constant. The magnetization component along the applied magnetic field direction is obtained from

$$M_{H}(T, H) = M_k \cos x + M_y \cos y + M_z \cos z, \quad (9)$$

where $x, y, z$ are the cosine directions of the applied magnetic field.

The entropy is considered as the sum of three main contributions: magnetic, lattice (phonons), and electronic. The magnetic entropy is calculated from the usual relation,

$$S_{mag}(T, H) = k_B \ln \left( \sum_i e^{-\varepsilon_i / k_BT} \right) + \frac{1}{T} \sum_i \varepsilon_i e^{-\varepsilon_i / k_BT} \quad (10)$$

The lattice entropy is obtained from Debye’s formula:

$$S_{lat}(T) = -3N_{ions} R \ln \left( 1 - e^{-\theta_D/T} \right) + 12N_{ions} R \left( \frac{\theta_D}{T} \right)^3 \int_0^{\theta_D/T} x^3 dx / e^x - 1. \quad (11)$$

where $N_{ions} = 2$ is the number of ions in the unit formula, $R$ the gas constant, and $\theta_D$ Debye’s temperature.

The electronic contribution to the entropy is calculated from the standard expression

$$S_{el}(T) = \bar{\sigma} \frac{\varepsilon}{T}, \quad (12)$$

where $\bar{\sigma}$ is the Sommerfeld coefficient.

The magnetocaloric quantities are obtained from the following relations:

$$\Delta S_T(T, H) = S_{tot}(T, H = 0) - S_{tot}(T, H \neq 0),$$
$$\Delta T_S(T, H) = T(S_{tot}, H \neq 0) - T(S_{tot}, H = 0). \quad (13)$$
III. RESULTS AND DISCUSSIONS

A. HoZn

In the calculations for the HoZn compound, we considered the total angular momentum \( J \) and the Landé factor \( g \) from Hund’s rules. The exchange parameter \( \lambda = 53.5 \text{ T}^2/\text{meV} \) was chosen to reproduce the Curie temperature. The CF parameters, \( x = 0.08 \) and \( W = 0.031 \text{ meV} \), and the quadrupolar coupling parameters, \( G_1 = -0.396 \times 10^{-3} \) and \( G_2 = 2.15 \times 10^{-3} \text{ meV} \) were extracted from Ref. 23. \( \tilde{g} = 10 \text{ mJ/mol K} \) and \( \theta_D = 173 \text{ K} \), were assumed as reported in Ref. 21. The calculations begin with the diagonalization of Hamiltonian (1), which is constructed within the \( \{ J = 8, M_J \} \) basis, followed by the self-consistent determination of the three magnetization components and of the five second-order operators mean values for each temperature and magnetic field. After obtaining these quantities, we proceed to calculate the specific heat, entropy and the magnetocaloric quantities.

Figure 1 shows the specific heat of HoZn at zero field. The solid line represents the calculations considering all the contributions to the Hamiltonian (exchange+CF+quadrupolar). The dotted line shows theoretical results considering only exchange and CF interactions \( (\lambda = 58 \text{ T}^2/\text{meV}, x = 0.67, \text{ and } W = 0.17 \text{ meV}) \). Note that in both cases the SRT (indicated by the arrow) is well reproduced. But the quadrupolar contribution is necessary to a correct description of the magnetization23 and of the magnetic excitations.29 Figure 2 shows the magnetization of HoZn vs \( H \) in the three main crystallographic directions at 4.2 K. Note the good agreement between theoretical calculations (solid, dashed, and dotted lines), obtained considering all contributions to Hamiltonian (1), and experimental results (open circles, squares, and triangles).

In our theoretical approach the SRT can be ascribed to a competition between the second-order operators averages. Note in Fig. 3, which shows the mean values of the second-order Stevens’ operators, that below the SRT temperature the only non-null averages are \( \langle O_2^0 \rangle \) and \( \langle P_{xy} \rangle \) and the magnetization points along the \( \langle 110 \rangle \) direction. At \( T_1 \) a discontinuous change is observed in which \( \langle O_2^0 \rangle \) vanishes, whereas the \( \langle P_{xy} \rangle \) assume the same value and consequently the magnetization rotates to the \( \langle 111 \rangle \) direction.

In Fig. 4 we have calculated the magnetization and the mean values of the second-order operators under several magnetic fields. Figures 4(a) and 4(b) show the results for the field applied along the \( \langle 110 \rangle \) direction. The discontinuity in the magnetization at \( T_{SR1}^{(110)} = 33 \text{ K} \), when \( \mu_B H = 1 \text{ T} \), is a consequence of a first-order SR transition, in which the magnetization direction changes from \( \langle 110 \rangle \) to an arbitrary direction \( \langle 100 \rangle \). As temperature increases \( M \) rotates back toward the \( \langle 110 \rangle \) direction in a second-order process at \( T_{SR2}^{(110)} = 68 \text{ K} \) (as indicated by the arrow in the figure). Note from the second-order operators averages that below \( T_{SR1}^{(110)} \) only \( \langle O_2^0 \rangle \) and \( \langle P_{xy} \rangle \) are non-null. At \( T_{SR1}^{(110)} \), \( \langle P_{yz} \rangle \) discontinuously appears and the first-order reorientation \( \langle 110 \rangle \rightarrow \langle 100 \rangle \) takes place. At \( T_{SR2}^{(110)} \) these averages vanish and therefore the second-order reorientation \( \langle 100 \rangle \rightarrow \langle 110 \rangle \) occurs. For an applied field of 3 T no spin reorientation is observed, as only \( O_2^0 \) and \( P_{xy} \) have non-null averages at any ordered temperature.

For the magnetic field in the \( \langle 100 \rangle \) direction [Figs. 4(c) and 4(d)] we observe two successive SRs when \( \mu_B H = 2 \text{ T} \). The first SR is of first-order type and the magnetization direction...
changes from \(\langle v \rangle_0\) to \(\langle v \rangle_o\) at \(T_{SR}^{(111)} = 34\) K (as indicated by the arrow). The second SR is of second-order type, and at \(T_{SR}^{(100)} = 70\) K the magnetization becomes parallel to the field. For \(\mu_0H = 9\) T it can be seen a kink in the \(M_H\) curve at 62 K, consequence of a second-order SR from an arbitrary direction \(\langle v \rangle_0\) toward the \(\langle 100 \rangle\) one. From the analysis of the second-order operators mean values we note that the first-order reorientation \(\langle v \rangle_0\) \(\rightarrow\) \(\langle v \rangle_o\) occurs when \(\langle P_{zy} \rangle, \langle P_{zx} \rangle\) becomes non-null, whereas the second-order SR \(\langle v \rangle_o\) \(\rightarrow\) \(\langle 100 \rangle\) takes place when \(\langle P_y \rangle = 0\) and \(|\langle O_2^0 \rangle| = |\langle O_2^1 \rangle|\) [see black lines and symbols in Fig. 4(b)].

Figures 4(e) and 4(f) show the results for the magnetic field along the \(\langle 111 \rangle\) direction. For \(\mu_0H = 0.3\) T a discontinuity in \(M_H\) is observed at \(T_{SR}^{(111)} = 16\) K (as indicated by the arrow) and it can be ascribed to a first-order SR from an arbitrary direction \(\langle v \rangle_o\) toward the \(\langle 111 \rangle\) one. Note from Fig. 4(b) that at \(T_{SR}^{(111)}\) the average of \(O_2^0\) vanishes, whereas \(\langle P_{xy} \rangle = \langle P_{yz} \rangle = \langle P_{zx} \rangle\) which leads to the SR. For \(\mu_0H = 2\) T no spin reorientation is observed, and at any ordered temperature the magnetization is parallel to the magnetic field.

Mapping the several above-described spin reorientations, which are consequences of the competition between the second-order operators, we built the spin reorientation diagram shown in Fig. 5. In Fig. 5(a), the magnetic fields were applied in the \(\langle 110 \rangle\) direction and SRs are observed for \(\mu_0H < 2.4\) T. In Fig. 5(b), the fields were applied along the \(\langle 100 \rangle\) direction, for \(\mu_0H > 9\) T the first-order SR at \(T_{SR1}\) vanishes and we observe only the second-order SR’s \(\langle v \rangle_0\) \(\rightarrow\) \(\langle 100 \rangle\). For magnetic fields in the \(\langle 111 \rangle\) direction [Fig. 5(c)] first-order SRs are observed for \(\mu_0H < 0.5\) T.

In what follows we analyze the influence of the various spin reorientations discussed previously on the magnetocaloric potentials \(\Delta S_f\) and \(\Delta T_f\).

Figure 6(a) shows the isothermal entropy change and Fig. 6(b) shows the adiabatic temperature change of HoZn versus temperature. The curves were obtained under a magnetic field intensity variation from 0 to 2 T using Eqs. (13) and (14). For the magnetic field applied along the \(\langle 111 \rangle\) direction one can note an inverse magnetocaloric effect below \(T_1\), the negative peak reaches the value \(-1.5\) J/kg K (\(-0.5\) K). A sign change occurs at \(T_1\), as indicated by the arrow, and increasing temperature \(-\Delta S_f\) \((\Delta T_f)\) reaches a maximum of 11.9 J/kg K (3.4 K) around \(T_C\). For the field in the \(\langle 110 \rangle\) direction we observe a discontinuity in the magnetocaloric potentials regarding the first-order SR at \(T_1\), which is followed by a table-like behavior between \(T_1\) and \(T_{SR1}^{(100)}\). At \(T_{SR1}^{(100)}\) a small discontinuity in \(-\Delta S_f\) \((\Delta T_f)\) occurs as a consequence of a first-order field-induced SR. With further increasing in temperature a kink can be seen at \(T_{SR2}^{(100)}\) (as indicated by the arrow), which is due to a second-order field-induced SR, see the spin reorientation diagram in Fig. 5(a). The peak in \(-\Delta S_f\) \((\Delta T_f)\) around \(T_C\) is 10.8 J/kg K.
Note that the spin reorientations were mapped from the analysis of the polar and azimuthal angles that the magnetization vector makes in respect to the Cartesian axes, i.e., \( \theta = \cos^{-1}\left(\frac{M_y}{\sqrt{M_x^2 + M_y^2}}\right) \) and \( \varphi = \tan^{-1}(M_x/M_y) \).

Figure 8 shows a spin reorientation diagram for ErZn. In Fig. 8(a) the field is along the \( \langle 110 \rangle \) direction. Below the SR line the magnetization points along an arbitrary direction \( \langle 110 \rangle \), between \( \langle 100 \rangle \) and \( \langle 110 \rangle \), and above the line it is parallel to the magnetic field. The SRs were observed for \( \mu_0 H \leq 3.6 \text{ T} \). When \( H \) is applied in the \( \langle 111 \rangle \) direction (Fig. 8) spin reorientations are predicted for fields lower than 2 T, and below the SR line the magnetization is in an arbitrary direction \( \langle 110 \rangle \).

We have also calculated the magnetocaloric effect for ErZn. Figure 9(a) shows the adiabatic temperature change of ErZn as a function of temperature. The calculations were performed for magnetic field intensity variations from 0 to 1 T, 0 to 3 T, and 0 to 5 T, in the \( \langle 100 \rangle \) (solid lines), \( \langle 110 \rangle \) (dashed lines), and \( \langle 111 \rangle \) (dotted lines) directions. We note that at the SR temperatures some kinks in the magnetocaloric quantities, which reflect the spin reorientations. For larger field variations, \( -\Delta S_T \) is observed only second-order SRs for ErZn. It should be mentioned that the spin reorientations are mapped from the analysis of the polar and azimuthal angles that the magnetization vector makes in respect to the Cartesian axes, i.e., \( \theta = \cos^{-1}\left(\frac{M_y}{\sqrt{M_x^2 + M_y^2}}\right) \) and \( \varphi = \tan^{-1}(M_x/M_y) \).

In the calculations for ErZn we used the following set of model parameters: \( \lambda = 18.5 \text{ T}^2/\text{meV} \), which was chosen to adjust the critical temperature \( T_C = 17 \text{ K} \); the CF parameters, \( x = 0.16 \) and \( W = 0.031 \text{ meV} \), and quadrupolar ones, \( G_1 = 0.129 \times 10^{-3} \text{ meV} \) and \( G_2 = 0.946 \times 10^{-3} \text{ meV} \), were assumed as in Ref. 23. The easy magnetization direction is \( \langle 100 \rangle \) at any temperature. The calculations of the magnetization in the three main cubic directions at 4.2 and 10 K are in good agreement with previous results. 23 As well as in HoZn, the application of magnetic fields in noneasy directions lead to field-induced SRs, which depend on the interaction balance represented by the competition between the second-order operator averages. It is worth noticing that we have observed only second-order SRs for ErZn. It should be mentioned that the spin reorientations were mapped from the analysis of the polar and azimuthal angles that the magnetization vector makes in respect to the Cartesian axes, i.e., \( \theta = \cos^{-1}\left(\frac{M_y}{\sqrt{M_x^2 + M_y^2}}\right) \) and \( \varphi = \tan^{-1}(M_x/M_y) \).

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In Table I the main characteristics of several magneto-caloric materials are given. The Tb-based compounds have the highest Curie temperatures, as expected for intermetallic compounds in which the critical temperatures scales with the de Gennes factor, \( \frac{g}{C_0} \left( \frac{J}{J+1} \right)^2 \). Note that despite the largest \( T_C \)'s, TbZn and TbCo\(_2\) have the lowest MCE peaks, which may occur for second-order magneto-caloric materials as the \( \Delta S_T \) peak around the phase transition varies as \( \frac{H}{T_C} \) (see Ref. 33, p. 25). The large MCE peaks of HoCo\(_2\) and ErCo\(_2\) is due to the first-order nature of their magnetic transition. It is worth noticing in Table I that despite the first-order transition around \( T_C \), the Co-based compounds with Ho and Er present a lower refrigerant capacity (RC) compared to HoZn, Ho\(_2\)In, and ErGa because for the latter the temperature interval considered to calculate RC spans over a wider range due to the spontaneous reorientation transition presented in these compounds. Among the RZn compounds, ErZn presents the lowest RC, which can be attributed to the absence of spontaneous reorientation transition.

### IV. FINAL COMMENTS

The magnetocaloric properties of HoZn and ErZn were discussed throughout a model Hamiltonian including the exchange, Zeeman, CF, and quadrupolar interactions. The spontaneous reorientation transition of HoZn at \( T_1 = 23 \) K

![Figure 7](image-url)  
**FIG. 7.** (Color online) Dependence of \(-\Delta S_T\) with \( \mu_0 M_H \) at the several spin reorientations temperatures and at \( T_C \), calculated in the (a) \( \langle 110 \rangle \), (b) \( \langle 100 \rangle \), and (c) \( \langle 111 \rangle \) directions.

![Figure 8](image-url)  
**FIG. 8.** Spin reorientation diagram for ErZn. The magnetic fields were applied (a) in the \( \langle 110 \rangle \) direction and (b) along the \( \langle 111 \rangle \) direction. The lines are guides for the eyes.

![Figure 9](image-url)  
**FIG. 9.** (Color online) (a) \(-\Delta S_T\) and (b) \( \Delta T_1 \) of ErZn calculated under several magnetic fields in the \( \langle 100 \rangle \) (solid lines), \( \langle 110 \rangle \) (dashed lines), and \( \langle 111 \rangle \) direction (dotted line).
TABLE I. Comparison of the magnetocaloric properties of some rare-earth-based intermetallic compounds.

<table>
<thead>
<tr>
<th></th>
<th>(T_C) (K)</th>
<th>(-\Delta S_{\text{mag}}^{\text{max}}) (J/kg K)</th>
<th>RC (J/kg)</th>
<th>(-\Delta S_{\text{mag}}^{\text{max}}) (J/kg K)</th>
<th>RC (J/kg)</th>
<th>Reference</th>
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