

**Magnetocaloric effect in rare-earth pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$** N. A. de Oliveira,<sup>1</sup> P. J. von Ranke,<sup>1</sup> and A. Troper<sup>1,2</sup><sup>1</sup>*Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier 524, Rio de Janeiro, 20550-013 Rio de Janeiro, Brazil*<sup>2</sup>*Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, Rio de Janeiro, 22290-180 Rio de Janeiro, Brazil*

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In this paper we study the magnetocaloric effect in the Laves phase pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ . We use a theoretical model, considering both the localized spins of rare-earth ions and the itinerant electrons of the transition elements. The two-body interactions are treated in the mean-field approach and the disorder is treated in the coherent-potential approximation. The calculated isothermal magnetic entropy and the adiabatic temperature change exhibit a good agreement with the available experimental data. We also propose a composite material, based on different samples of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ , to work as a magnetic refrigerant in the Ericsson cycle in the temperature range from 15 K to 36 K.

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**I. INTRODUCTION**

The magnetic cooling or heating occurs when a magnetic material is submitted to an external magnetic-field change, in an ideal thermodynamical cycle<sup>1,2</sup> such as the Carnot cycle in the entropy versus temperature diagram. In the isothermal processes of this cycle, which are generated by increasing or decreasing the external magnetic field, keeping constant the temperature, the magnetic part of the entropy of the material is then changed by  $\Delta S_{mag}(T) = S_{mag}(T, h^{ext} \neq 0) - S_{mag}(T, h^{ext} = 0)$ . The quantity  $\Delta S_{mag}$  is usually called the isothermal magnetic entropy change. In the adiabatic processes of this cycle which are generated by increasing or decreasing the external magnetic field, keeping constant the entropy, the temperature of the magnetic material is then changed by  $\Delta T_{ad}(T) = T_2 - T_1$ , determined under the adiabatic condition  $S(T_2, h^{ext} \neq 0) = S(T_1, h^{ext} = 0)$ , where  $S$  is the total entropy. The magnetocaloric effect, which is measured by both  $\Delta S_{mag}(T)$  and  $\Delta T_{ad}(T)$ , is intrinsic to all magnetic materials and is due to the coupling of the magnetic lattice with the external magnetic field. The magnetocaloric effect has been investigated in many magnetic materials.<sup>1-11</sup> The heavy lanthanide metals and their compounds have been the most studied materials because of their large magnetic moments. On the one hand, the theoretical description of the magnetocaloric effect in rare earth intermetallic compounds such as  $\text{RAl}_2$  and  $\text{RNi}_2$  may be done by means of a model Hamiltonian<sup>12-14</sup> including only local spins, since Al and Ni are nonmagnetic and the magnetism of these intermetallics is entirely due to the rare-earth ions. On the other hand, the theoretical description of the magnetocaloric effect in  $\text{RCO}_2$  and  $\text{RFe}_2$  intermetallic compounds<sup>15,16</sup> should include both localized  $4f$  spins and itinerant  $3d$  electrons, since in these compounds the magnetic moments at the  $R$ ,  $\text{Co}$ , and  $\text{Fe}$  sites contribute to the magnetism. However, it should be emphasized that the theoretical description of the magnetocaloric effect in  $\text{RCO}_2$  compounds is somewhat easier than that for the  $\text{RFe}_2$  compounds; once in the  $\text{RCO}_2$  intermetallics the magnetic moments at the  $\text{Co}$  sites are induced by the rare-earth ions, whereas in the  $\text{RFe}_2$  compounds both the  $R$  and the  $\text{Fe}$  ions have spontaneous magnetic moments.

To what extent the itinerant electrons participate in the physical mechanism which governs the magnetocaloric effect in rare-earth-transition-element intermetallic compounds is not yet completely understood. Experimental data<sup>10</sup> show that both the isothermal magnetic entropy change and the adiabatic temperature change in the intermetallic compounds  $\text{RCO}_2$  ( $R = \text{Er}, \text{Dy}, \text{Ho}$ ) exhibit large values at around the magnetic ordering temperature and they both drop quickly further way. This kind of behavior in the  $\Delta S_{mag}$  versus  $T$  and  $\Delta T_{ad}$  versus  $T$  curves is directly associated with the first-order magnetic phase transition due to the metamagnetism at the  $3d$  band of  $\text{Co}$ . Although the main contribution to the magnetic and thermodynamical properties of the  $\text{RCO}_2$  intermetallic compounds comes from the local spins of the rare-earth ions, the itinerant electrons of the  $\text{Co}$  ions play an important role in them. Experimental data<sup>11</sup> also show that the substitution of  $\text{Ni}$  for  $\text{Co}$  in the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  not only reduces the magnetic ordering temperature but also changes the nature of the magnetic phase transition from first to second order, above a critical  $\text{Ni}$  concentration at around 10%. Accordingly, the magnitude and the position of the peak in the  $\Delta S_{mag}$  versus  $T$  and  $\Delta T_{ad}$  versus  $T$  curves change as a function of the  $\text{Ni}$  concentration. As it has been mentioned before, the magnetocaloric effect in  $\text{ErNi}_2$  is entirely due to the local moments of  $\text{Er}$  ions while in  $\text{ErCo}_2$  both itinerant electrons and local spins play an important role in the establishment of the magnetocaloric effect. Hence for a small  $\text{Ni}$  concentration the magnetocaloric effect in the doped compound  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  is due to two magnetic sublattices associated with local spins and itinerant electrons. As the  $\text{Ni}$  concentration is increased the contribution of the itinerant electrons to the total magnetization decreases, so that the magnetocaloric effect is mainly governed by the local spins of the  $\text{Er}$  ions.

In order to study the magnetocaloric effect in the Laves phase pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  we use a microscopic model Hamiltonian considering that the local spins of the  $\text{Er}$  ions are immersed into an effective subsystem of itinerant electrons containing disorder. We also include the effect of the crystalline electrical field on the  $4f$  spins of the rare-

earth ions. For the sake of simplicity we use the Hartree-Fock approximation to treat the Coulomb interaction between itinerant electrons and the molecular-field approximation to deal with the exchange interaction between localized spins. The disorder is treated in the nondiagonal coherent-potential approximation. The calculated  $\Delta S_{mag}$  versus  $T$  and  $\Delta T_{ad}$  versus  $T$  curves for the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  are in good agreement with the available experimental data.<sup>11</sup> We also propose a composite material, formed by six different samples of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  ( $c=0.0, 0.012, 0.025, 0.035, 0.05, 0.075$ ) to work as a magnetic refrigerant from 15 K to 36 K.

## II. HAMILTONIAN AND APPROXIMATIONS

In order to describe the magnetocaloric effect in the pseudobinary compound  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ , we start with the following model Hamiltonian:

$$\begin{aligned}
H = & -J_0^{eff} \sum_{ij} J_i^f J_j^f - g_i \mu_B \sum_i J_i^f h^{ext} - J_{df} \sum_i J_i^f s_i^d \\
& + \sum_i W \left[ x \frac{(O_4^0 + 5O_4^4)_i}{F_4} + (1-|x|) \frac{(O_6^0 - 21O_6^4)_i}{F_6} \right] \\
& + \sum_{i\sigma} \varepsilon_{0\sigma}^I d_{i\sigma}^+ d_{i\sigma} + \sum_{ij\sigma} T_{ij\sigma}^{II'} d_{i\sigma}^+ d_{j\sigma} + U^I \sum_i n_{i\uparrow} n_{i\downarrow} \\
& - g_e \mu_B \sum_i s_i^d h^{ext}. \tag{1}
\end{aligned}$$

The terms in the first row of this Hamiltonian describe localized spins, where  $J^f$  is the total angular momentum of the rare-earth ions and  $h^{ext}$  represents the external magnetic field applied along the easy magnetization direction.  $J_0^{eff}$  is the effective exchange interaction parameter between localized spins. The terms in the second row of this Hamiltonian represent the crystalline electrical field for the cubic symmetry,<sup>17</sup> where  $W$  is an energy scale and  $x$  gives the relative importance of the fourth- and sixth-order terms.  $O_m^n$  are Stevens' operators<sup>18</sup> and  $F_4=60$ ,  $F_6=13860$ . The terms in the third and fourth row of this Hamiltonian describe itinerant electrons where  $\varepsilon_{0\sigma}^I$  ( $I=\text{Co}$  or  $\text{Ni}$ ) is an atomic energy level and  $T_{ij\sigma}^{II'}$  ( $I, I'=\text{Co}$  or  $\text{Ni}$ ) represents the electron hopping energy between two different sites;  $U^I$  ( $I=\text{Co}$  or  $\text{Ni}$ ) is the Coulomb interaction parameter between itinerant electrons;  $s_i^d$  is the spin of itinerant electrons and  $J_{df}$  is the exchange interaction parameter between itinerant electrons and localized spins. The parameters  $g_i$  and  $g_e$  are the Landé factors of the rare-earth ions and of the itinerant electrons, respectively. Note that in this Hamiltonian, the disorder is contained in the local terms  $\varepsilon_{0\sigma}^I$  and  $U^I$  as well as in the nonlocal term  $T_{ij\sigma}^{II'}$ . In the mean-field approximation the Hamiltonian (1) can be written as two effective Hamiltonians, namely:

$$H_d^{eff} = \sum_{i\sigma} \varepsilon_{i\sigma}^I d_{i\sigma}^+ d_{i\sigma} + \sum_{ij\sigma} T_{ij\sigma}^{II'} d_{i\sigma}^+ d_{j\sigma}, \tag{2}$$

$$\begin{aligned}
H_f^{eff} = & - \sum_i (J_0^{eff} \langle J^f \rangle + 0.5 J_{df} \langle s^d \rangle) J_i^f + H^{CF} \\
& - g_i \mu_B \sum_i h^{ext} J_i^f. \tag{3}
\end{aligned}$$

The Hamiltonian  $H_d^{eff}$  describes a subsystem of itinerant electrons under the action of the effective magnetic field generated by the localized spins, where  $\varepsilon_{i\sigma}^I = \varepsilon_0^I + U^I \langle n_{-\sigma} \rangle - 0.5 \sigma J_{df} \langle J^f \rangle - g_e \mu_B h^{ext}$ . The effective Hamiltonian  $H_f^{eff}$  describes a subsystem of localized spins under the action of the crystalline electric field ( $H^{CF}$ ) and coupled to the itinerant electrons.

In order to treat the disorder in the effective Hamiltonian  $H_d^{eff}$ , we use the coherent-potential approximation (CPA).<sup>19</sup> In this approximation, we consider that the difference in the electron hopping energy involving sites occupied by different atoms is parametrized by

$$T_{ij}^{II'} = \xi_i^I T_0 \xi_j^{I'}, \tag{4}$$

where  $T_0$  is a reference hopping energy. The parameters  $\xi_i^I$  and  $\xi_j^{I'}$  ( $I, I'=\text{Co}$  or  $\text{Ni}$ ) should be taken consistently with the extension of the  $d$ -wave functions of Co and Ni atoms. With this approximation we can write Green's function  $G(z) = (z - H_d^{eff})^{-1}$  as<sup>19</sup>

$$G_\sigma(z) = \left[ \sum_{i\sigma} (z - \varepsilon_{i\sigma}^I) d_{i\sigma}^+ d_{i\sigma} - \sum_{ij\sigma} \xi_i^I T_0 \xi_j^{I'} d_{i\sigma}^+ d_{j\sigma} \right]^{-1}, \tag{5}$$

where  $z = \varepsilon + i0$ . Defining the renormalized energy  $\tilde{\varepsilon}_{i\sigma}^I = (z - \varepsilon_{i\sigma}^I) / \xi_i^2$  the Green function reads

$$G_\sigma(z) = \frac{1}{(\xi^I)^2} \left[ \sum_{i\sigma} \tilde{\varepsilon}_{i\sigma}^I(z) d_{i\sigma}^+ d_{i\sigma} - \sum_{ij\sigma} T_0 d_{i\sigma}^+ d_{j\sigma} \right]^{-1}. \tag{6}$$

Note that in the above Green function, the disorder is now contained only in the local term described by the renormalized energy  $\tilde{\varepsilon}_{i\sigma}^I$ . In order to restore the translational invariance of the system, we introduce an effective medium with a self energy  $\Sigma_\sigma$ . The Green function of the subsystem of itinerant electrons, written in terms of the self-energy, is given by

$$g_\sigma(z) = \left[ \sum_{i\sigma} \Sigma_\sigma(z) d_{i\sigma}^+ d_{i\sigma} - \sum_{ij\sigma} T_0 d_{i\sigma}^+ d_{j\sigma} \right]^{-1}. \tag{7}$$

In order to determine the self-energy, we put in a given site “0” an atom with energy  $\tilde{\varepsilon}_{i\sigma}^I$ , creating a Koster-Slater problem of a single impurity embedded in the effective medium. The perturbed Green function  $\Gamma(z)$  for the Koster-Slater problem in the effective medium is

$$\Gamma_{\sigma}(z) = \left\{ \left[ \sum_{i\sigma} \Sigma_{\sigma}(z) d_i^+ d_i - \sum_{ij\sigma} T_0 d_i^+ d_j \right] + (\tilde{\varepsilon}'_{0\sigma}(z) - \Sigma_{\sigma}(z)) d_0^+ d_0 \right\}^{-1}. \quad (8)$$

Using the unperturbed Green function

$$g_{\sigma}(z) = \left[ \sum_{i\sigma} i\sigma \Sigma_{\sigma} d_{i\sigma}^+ d_{i\sigma} - \sum_{ij\sigma} T_0 d_{i\sigma}^+ d_{j\sigma} \right]^{-1}$$

we can rewrite the perturbed Green function  $\Gamma(z)$  as

$$\Gamma_{\sigma}(z) = \{ [g_{\sigma}^{-1}(z) + (\tilde{\varepsilon}'_{0\sigma}(z) - \Sigma_{\sigma}(z))] \}^{-1}. \quad (9)$$

Multiplying on the left by the inverse of term on the right-hand side and after a simple algebra, the perturbed Green function  $\Gamma(z)$ , written in the site representation, takes the form

$$\begin{aligned} \Gamma_{ij\sigma}(z) &= g_{ij\sigma}(z) \\ &+ g_{i0\sigma}(z) \frac{(\Sigma_{\sigma}(z) - \tilde{\varepsilon}'_{0\sigma}(z))}{1 - g_{00\sigma}(z)(\Sigma_{\sigma}(z) - \tilde{\varepsilon}'_{0\sigma}(z))} g_{0j\sigma}(z). \end{aligned} \quad (10)$$

Taking the average on the previous equation and assuming  $\langle \Gamma_{ij\sigma}(z) \rangle = \langle g_{ij\sigma}(z) \rangle$ , we obtain the well-known CPA equation<sup>19</sup>

$$\left\langle \frac{(\Sigma_{\sigma}(z) - \tilde{\varepsilon}'_{0\sigma}(z))}{1 - g_{00\sigma}(z)(\Sigma_{\sigma}(z) - \tilde{\varepsilon}'_{0\sigma}(z))} \right\rangle = 0 \quad (11)$$

which determines the self-energy  $\Sigma_{\sigma}$ . Here  $g_{00\sigma}$  can be calculated by the Hilbert transform of a standard paramagnetic  $3d$  density of states  $\rho_0$ , i.e.,  $g_{00\sigma}(z) = \int d\varepsilon \rho_0(\varepsilon)/(z - \Sigma_{\sigma})$ . Once the self-energy is determined, the local Green function at the impurity site 0 occupied by an atom  $I$  ( $I = \text{Co}$  or  $\text{Ni}$ ) is given by

$$\Gamma_{00\sigma}^I(z) = \left[ \frac{g_{00\sigma}(z)}{1 - g_{00\sigma}(z)(\Sigma_{\sigma}(z) - \tilde{\varepsilon}'_{0\sigma}(z))g_{00\sigma}(z)} \right]. \quad (12)$$

Accordingly, the spin-polarized local density of states at the origin occupied by an atom  $I$  is then given by

$$\rho_{\sigma}^I(\varepsilon) = -\frac{1}{\pi} \text{Im} \left[ \frac{1}{(\xi^I)^2} \Gamma_{00\sigma}^I(z) \right]. \quad (13)$$

### III. MAGNETIZATION AND ENTROPY

The total magnetization of the intermetallic compound is given by the summation of the contribution from the subsystem of itinerant electrons ( $M^d$ ) and the contribution from the subsystem of localized spins ( $M^R$ ). The temperature dependence of the magnetization associated with the subsystem of localized spins is given by

$$M^R = g_i \mu_B \frac{\sum_i \langle \phi_i | J | \phi_i \rangle \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}, \quad (14)$$

where  $\beta = 1/kT$ ,  $k$  being the Boltzmann constant.  $\phi_i$  and  $E_i$  are the eigenvectors and the eigenvalues of the effective Hamiltonian  $H_i^{eff}$ .

The local magnetization at the Co or Ni site is calculated by  $M^I = n_{\uparrow}^I - n_{\downarrow}^I$ , where  $n_{\sigma}^I$  is the electron occupation number per spin direction given by

$$n_{\sigma}^I = \int_{-\infty}^{\mu} \rho_{\sigma}^I(\varepsilon) f(\varepsilon) d\varepsilon. \quad (15)$$

Here  $f(\varepsilon)$  is the Fermi distribution function,  $\mu$  is the chemical potential, and  $\rho_{\sigma}^I(\varepsilon)$  is the local density of states at a site occupied by an atom  $I$  ( $I = \text{Co}$  or  $\text{Ni}$ ), calculated by Eq. (13). The magnetization in the subsystem of itinerant electrons is then calculated by  $M^d = (1-c)M^{\text{Co}} + cM^{\text{Ni}}$ . Note that the contribution from the itinerant electrons to the total magnetization depends on the local spins through  $\langle J^f \rangle$  which renormalizes the density of states  $\rho_{\sigma}^I$ . Note also that the contribution from the localized spins to the total magnetization depends on the itinerant electrons via  $\langle s^d \rangle$  which acts on the subsystem of local spins as an effective magnetic field.

The total entropy of the intermetallic compounds is made by the contribution from the magnetic ( $S_{mag}$ ) and the crystalline lattices ( $S_{lat}$ ), i.e.,  $S_{tot} = S_{lat} + S_{mag}$ . Here we take the crystalline lattice entropy in the Debye approximation, which is given by

$$\begin{aligned} S_{lat}(T) &= \left[ -3R \ln \left( 1 - \exp \left( -\frac{\Theta_D}{T} \right) \right) \right. \\ &\left. + 12R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{\exp(x) - 1} dx \right], \end{aligned} \quad (16)$$

where  $\Theta_D$  is the Debye temperature and  $R$  is the universal gas constant. The magnetic entropy  $S_{mag}$  is the sum of the contribution from the subsystem of localized spins ( $S_{loc}$ ) plus the contribution from the subsystem of itinerant electrons ( $S_{el}$ ), i.e.,  $S_{mag} = S_{loc} + S_{el}$ . The contributions  $S_{loc}$  and  $S_{el}$  are given respectively by the relations<sup>14-16</sup>

$$S_{loc}(T, h^{ext}) = R \left[ \ln \sum_i e^{-\beta E_i} + \frac{1}{kT} \frac{\sum_i i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \right], \quad (17)$$

$$\begin{aligned} S_{el}(T, h^{ext}) &= R \left[ \sum_{\sigma} \int \ln(1 + e^{-\beta(\varepsilon - \mu)}) \rho_{\sigma}(\varepsilon) d\varepsilon \right. \\ &\left. + \frac{1}{kT} \sum_{\sigma} \int (\varepsilon - \mu) \rho_{\sigma}(\varepsilon) f(\varepsilon) d\varepsilon \right]. \end{aligned} \quad (18)$$

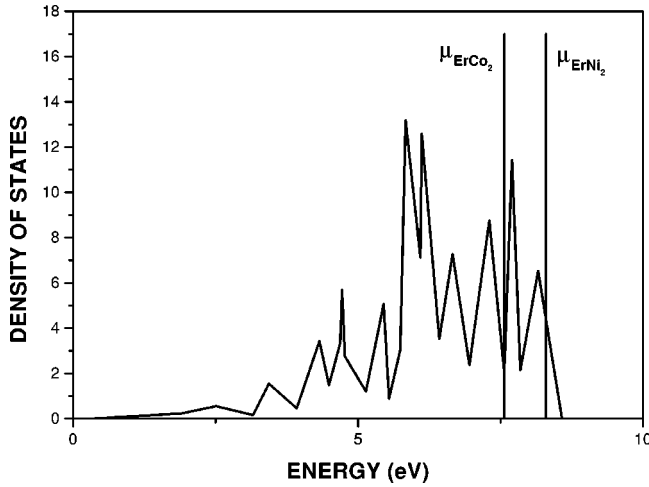


FIG. 1. Paramagnetic density of states for the intermetallic compounds  $\text{ErCo}_2$  and  $\text{ErNi}_2$ . Vertical lines represent the chemical potentials.

Once the total entropy is obtained the magnetic entropy change and the adiabatic temperature change upon magnetic field variation is calculated by

$$\Delta S_{mag}(T) = S_{mag}(T, h^{ext} \neq 0) - S_{mag}(T, h^{ext} = 0), \quad (19)$$

$$\Delta T_{ad}(T) = T_2 - T_1. \quad (20)$$

#### IV. NUMERICAL RESULTS AND DISCUSSION

In this section we show our theoretical calculations for the magnetocaloric effect in the Laves phase pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ . The Debye temperature for the intermetallic compounds  $\text{ErCo}_2$  and  $\text{ErNi}_2$  were respectively taken as<sup>12,20</sup>  $\Theta_D^{\text{Co}} = 240$  K and  $\Theta_D^{\text{Ni}} = 200$  K. The crystal-field parameters for the intermetallic compounds  $\text{ErCo}_2$  and  $\text{ErNi}_2$  were respectively taken as<sup>21,22</sup> [ $x^{\text{Co}} = -0.24$ ,  $W^{\text{Co}} = -0.042$  meV] and [ $x^{\text{Ni}} = -0.54$ ,  $W^{\text{Ni}} = -0.034$  meV]. For intermediate concentrations we take these parameters as a linear interpolation of the corresponding values for the pure compounds. The total angular momentum  $J^f$  and the  $g$  factors were extracted from Hund's rule. The exchange interaction parameter  $J_{df}$  was taken as<sup>23</sup>  $J_{df} = 1.4$  meV. For a given Ni concentration, the effective exchange interaction parameter  $J_0^{eff}$  was properly chosen to describe the experimental value of the magnetic ordering temperature of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ . The standard paramagnetic  $3d$  density of states for the pure intermetallic compound  $\text{ErCo}_2$  ( $c=0$ ) was taken from the calculations of Syshchenko *et al.*<sup>24</sup> (see Fig. 1). The  $3d$ -electron occupation number at the Co site in  $\text{ErCo}_2$  was estimated as  $n^{\text{Co}} = 1.80$ . For the pure intermetallic compound  $\text{ErNi}_2$  ( $c=1.0$ ) we consider the starting paramagnetic  $3d$  density of states, similar to the one used for the pure compound  $\text{ErCo}_2$  with slightly different bandwidth. The  $3d$ -electron occupation number at the Ni site in  $\text{ErNi}_2$  was estimated as  $n^{\text{Ni}} = 1.96$ . In the intermetallic  $\text{ErCo}_2$ , the Fermi level lies close to a sharp peak in the density of states, whereas in the intermetallic  $\text{ErNi}_2$ , it is located at the end of

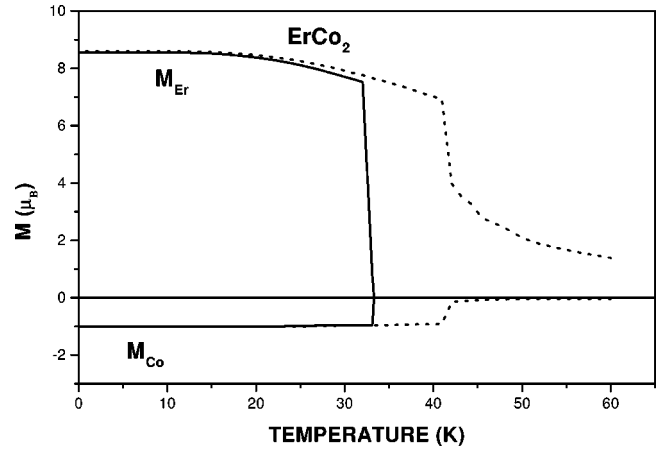


FIG. 2. Temperature dependence of the local magnetization in the Laves phase compound  $\text{ErCo}_2$ . The solid lines represent the local magnetization in the absence of an external magnetic field. The dotted lines represent the local magnetization calculated with an external magnetic field of 5 T.

the  $3d$  band as can be seen in Fig. 1. In our model the difference in the Co and Ni bandwidth is taken into account by the parameter  $\xi^I$  ( $I = \text{Co}$  or  $\text{Ni}$ ). Here we take  $\xi^{\text{Co}} = 1$  and  $\xi^{\text{Ni}} = 1.15$ . The factor  $U^I$  parametrizing the Coulomb interaction between itinerant electrons was chosen to ensure that the Stoner criterion for the appearance of the magnetic order at the Co or Ni site is not fulfilled. All of these parameters are kept fixed during the entire self-consistent process.

In order to solve the self-consistency defined by the coupling between the subsystems of localized spins and itinerant electrons, we take the following procedure. For a given temperature and for a initial value of  $\langle s^d \rangle$  we write the effective Hamiltonian  $H_f^{eff}$  for the subsystem of localized spins in a matrix notation<sup>18</sup> using the eigenvectors of the crystal-field term in the cubic symmetry for  $J = 15/2$ . After diagonalizing this matrix, we obtain the energy eigenvalues and the mean value  $\langle J^f \rangle$ . Afterwards we turn to the subsystem of itinerant electrons and use the obtained value of  $\langle J^f \rangle$  to compute the spin-polarized density of states and consequently obtain a new value for  $\langle s^d \rangle$ . This process is repeated until two consecutive values of  $\langle s^d \rangle$  and  $\langle J^f \rangle$  are obtained within a precision previously defined. After solving the process consistently, we calculate the magnetization and the total entropy of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  in the absence of an external magnetic field and for  $h^{ext} = 5$  T. Our calculations show that in the case of the pure compound  $\text{ErCo}_2$  the subsystem of localized spins has a spontaneous magnetization due to the exchange coupling between local spins. On the other hand, the magnetic subsystem of itinerant electrons has a magnetization antiparallel to the Er one, induced by the coupling of the itinerant electrons with the local spins. In Fig. 2, we show the temperature dependence of the contributions from the subsystems of local spins and itinerant electrons to the total magnetization of the intermetallic compound  $\text{ErCo}_2$ . The nature of the magnetic phase transition at around  $T_c = 33$  K is of first order. This first-order transition is due to the metamagnetic transition at the Co band, which is associated with the position of the Fermi level near a sharp

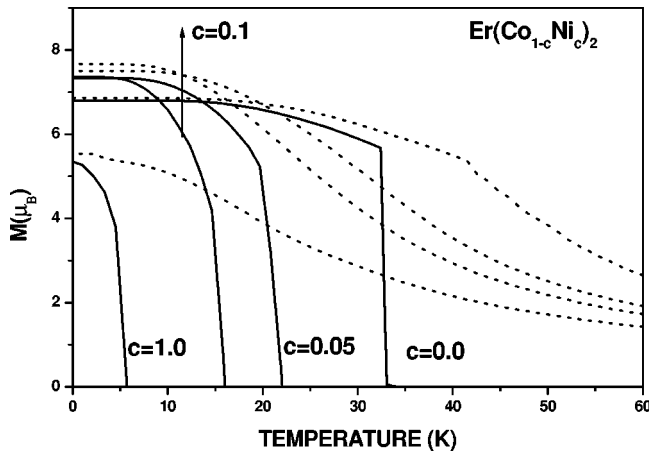


FIG. 3. Temperature dependence of the total magnetization, per unit formula, in the Laves phase pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ . The solid lines represent the total magnetization calculated in the absence of an external magnetic field, whereas the dotted lines represent the local magnetization calculated with an external magnetic field of 5 T.

peak in the density of states. As Ni is substituted for Co the 3*d*-electron occupation number increases and the Fermi energy moves away from the peak in the density of states. As a result, the contribution from the 3*d* band to the total magnetization decreases gradually. Besides, the critical temperature drops with increasing Ni concentration, and the magnetic phase transition becomes of second order, above a critical Ni concentration. In Fig. 3, we show the temperature dependence of the total magnetization, per unit formula, of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  for some Ni concentrations. In Fig. 4 we plot the magnetic entropy for the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ , in the absence of an external magnetic field, as well as for an external magnetic field of 5 T. From this figure we can observe that the magnetic entropy of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  for all Ni concentrations saturates around  $R \ln(2J+1) \approx 22.98$  J/K mol, which is the expected saturation value of the magnetic entropy for the 4*f* spins of the Er ions. This fact indicates that the contribution from the itinerant electrons to the magnetic entropy of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  at high temperature is almost negligible. However, the first-order magnetic phase transition observed in this pseudobinary, with a latent heat of about 346 J/mol, for  $c=0$  and 125 J/mol for  $c=0.05$  and its influence on the magnetocaloric effect strongly depends on the coupling between itinerant 3*d* electrons and local 4*f* spins.

We calculate the isothermal magnetic entropy and the adiabatic temperature change for the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  using a magnetic-field variation from 0 to 5 T. The obtained results are shown in Figs. 5 and 6, respectively. The curves for  $c=0.025$  are our theoretical predictions, since there are no available experimental data for this concentration. For the other concentrations, our calculations are in agreement with the experimental data.<sup>11</sup> However, we can note some deviations of our calculations in the low-temperature regime for some Ni concentrations. This means that the model should be improved to calculate better the electronic structure, which plays an important role in the

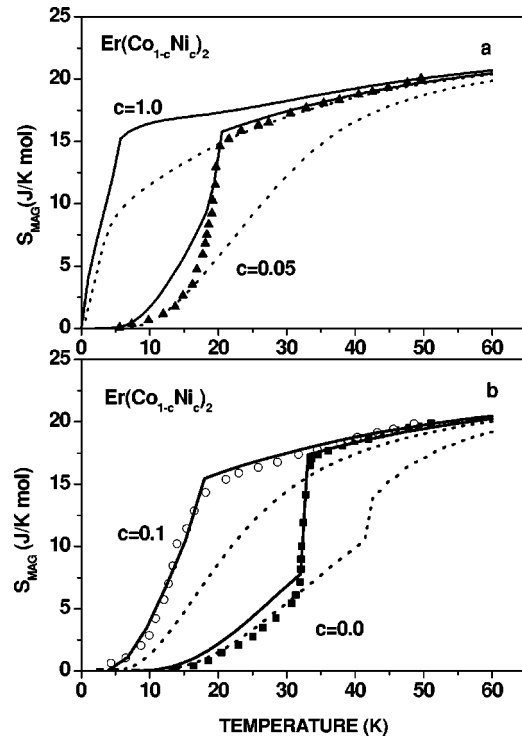


FIG. 4. Temperature dependence of the magnetic entropy in the Laves phase pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  for  $c=1.0$ ,  $c=0.05$  (a) and  $c=0.1$ ,  $c=0.0$  (b). The solid lines correspond to our calculations in the absence of an external magnetic field, whereas open circles, triangles, and squares represent experimental data (Ref. 11). The dotted lines correspond to our calculations for an external magnetic field of 5 T.

magnetocaloric effect of this pseudobinary.

From Figs. 5 and 6, we can observe that both the  $\Delta S_{\text{mag}}$  versus  $T$  and  $\Delta T_{\text{ad}}$  versus  $T$  curves of the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  for small Ni concentrations exhibit the maximum value at around the magnetic ordering temperature and

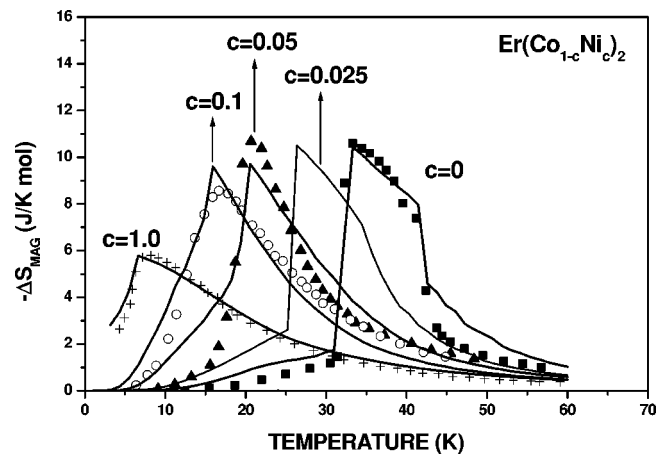


FIG. 5. Temperature dependence of the isothermal magnetic entropy change in the Laves phase pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ . The solid lines correspond to our calculations for a magnetic-field variation from 0 to 5 T. Open circles, triangles, squares, and crosses represent experimental data (Ref. 11).

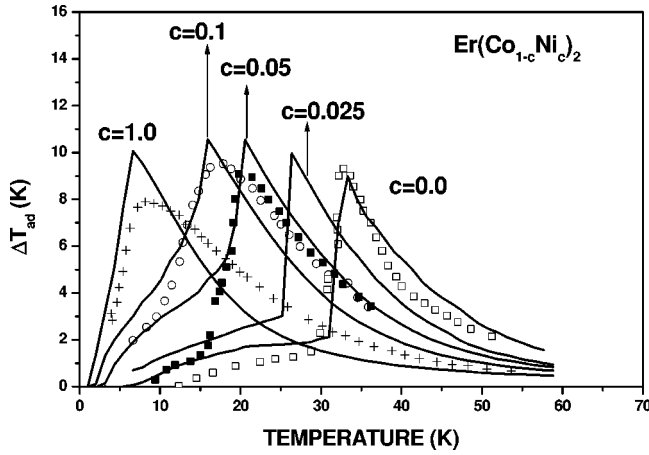


FIG. 6. Temperature dependence of the adiabatic temperature change in the Laves phase pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ . The solid lines correspond to our calculation for a magnetic-field variation from 0 to 5 T. Open circles, triangles, squares, and crosses represent experimental data (Ref. 11).

drop down quickly as we move further away. Besides, the position of the maximum value of the  $\Delta S_{mag}$  versus  $T$  and  $\Delta T_{ad}$  versus  $T$  curves moves to lower temperature as we increase the Ni concentration. The existence of large values in the  $\Delta S_{mag}$  versus  $T$  and  $\Delta T_{ad}$  versus  $T$  curves only at around the magnetic ordering temperature imposes a hard limitation to the use of single magnetic materials as a good magnetic refrigerant in the Ericsson thermodynamical cycle. In order to overcome this limitation the creation of a composite material made by combining single magnetic materials with slightly different magnetic ordering temperature but with similar magnitude of the isothermal magnetic entropy change has been suggested in the literature.<sup>25,26</sup> The composite magnetic material obtained in this way is supposed to exhibit a nearly constant isothermal magnetic entropy change in a wider range of temperature. Here, we use numerical simulations to construct a composite material formed by  $[\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2]_{y_i}$  ( $c=0.0, 0.012, 0.025, 0.035, 0.05, 0.075$ ), i.e.,  $A_{y_1}B_{y_2}C_{y_3}D_{y_4}E_{y_5}F_{y_6}$ , where  $A=\text{ErCo}_2$ ,  $B=\text{Er}(\text{Co}_{0.988}\text{Ni}_{0.012})_2$ ,  $C=\text{Er}(\text{Co}_{0.975}\text{Ni}_{0.025})_2$ ,  $D=\text{Er}(\text{Co}_{0.965}\text{Ni}_{0.035})_2$ ,  $E=\text{Er}(\text{Co}_{0.95}\text{Ni}_{0.05})_2$ , and  $F=\text{Er}(\text{Co}_{0.925}\text{Ni}_{0.075})_2$ . The factors  $y_i$  represent the mass ratio of each component under the condition  $y_1+y_2+y_3+y_4+y_5+y_6=1$ . The effective isothermal magnetic entropy change and the magnetization of this composite material is given by<sup>26</sup>

$$(\Delta S_{mag})_{comp} = \sum_{i=1}^6 y_i (\Delta S_{mag})_i,$$

$$M_{comp} = \sum_{i=1}^6 y_i M_i,$$

where  $M_i$  and  $(\Delta S_{mag})_i$  ( $i=1,2,3,4,5,6$ ) represent the magnetization and the effective isothermal magnetic entropy change of the single materials  $\text{ErCo}_2$ ,  $\text{Er}(\text{Co}_{0.988}\text{Ni}_{0.012})_2$ ,  $\text{Er}(\text{Co}_{0.975}\text{Ni}_{0.025})_2$ ,  $\text{Er}(\text{Co}_{0.965}\text{Ni}_{0.035})_2$ ,  $\text{Er}(\text{Co}_{0.95}\text{Ni}_{0.05})_2$ ,

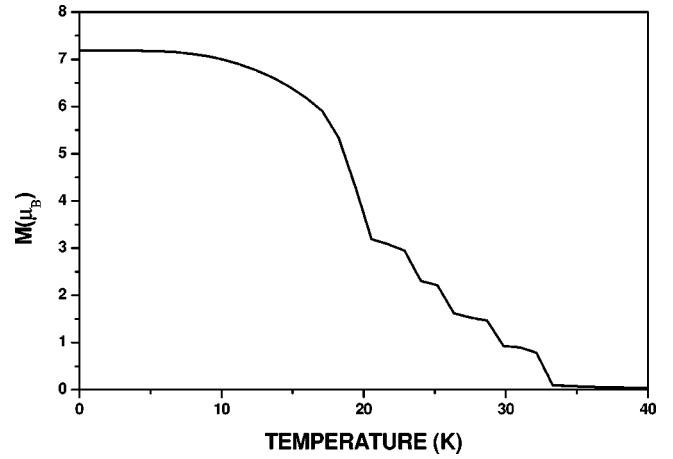


FIG. 7. Temperature dependence of the magnetization of the composite material  $A_{0.14}B_{0.09}C_{0.11}D_{0.12}E_{0.26}F_{0.28}$ , where  $A=\text{ErCo}_2$ ,  $B=\text{Er}(\text{Co}_{0.988}\text{Ni}_{0.012})_2$ ,  $C=\text{Er}(\text{Co}_{0.975}\text{Ni}_{0.025})_2$ ,  $D=\text{Er}(\text{Co}_{0.965}\text{Ni}_{0.035})_2$ ,  $E=\text{Er}(\text{Co}_{0.95}\text{Ni}_{0.05})_2$ , and  $F=\text{Er}(\text{Co}_{0.925}\text{Ni}_{0.075})_2$ .

and  $\text{Er}(\text{Co}_{0.925}\text{Ni}_{0.075})_2$ , respectively. The temperature dependence of the total magnetization of this composite material, calculated using  $y_1=0.14$ ,  $y_2=0.09$ ,  $y_3=0.11$ ,  $y_4=0.12$ ,  $y_5=0.26$ , and  $y_6=0.28$  is shown in Fig. 7. The steps observed in this magnetization curve are due to the superposition of the magnetization curves of each single material which exhibits first-order magnetic phase transition at different magnetic ordering temperature. Associated to each step in this magnetization curve, there are peaks in the  $\Delta S_{mag}$  versus  $T$  and  $\Delta T_{ad}$  versus  $T$  curves. This is easily understood, if we invoke that both  $\Delta S_{mag}$  and  $\Delta T_{ad}$  can be calculated by the derivative of the magnetization curve with respect to temperature, i.e.,  $\Delta S_{mag} = \int (\partial M / \partial T) dh^{ext}$   $\Delta T_{ad} = - \int (T/C) (\partial M / \partial T) dh^{ext}$ , where  $C$  is the specific heat. The corresponding  $\Delta S_{mag}$  versus  $T$  curve of this composite material is shown in Fig. 8. From this figure, we can observe

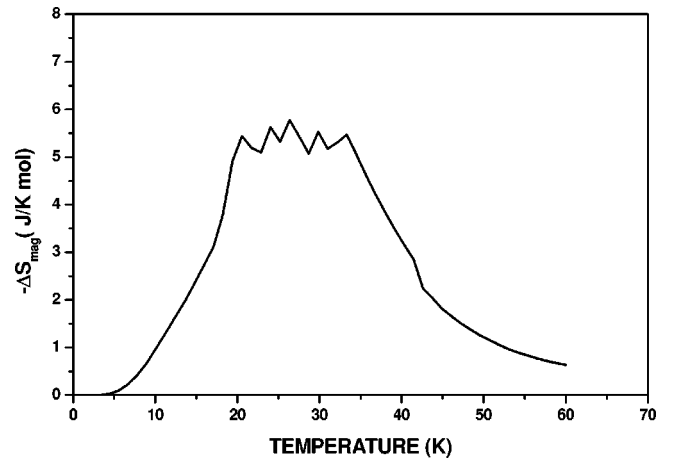


FIG. 8. Temperature dependence of the isothermal magnetic entropy change in the composite material  $A_{0.14}B_{0.09}C_{0.11}D_{0.12}E_{0.26}F_{0.28}$ , where  $A=\text{ErCo}_2$ ,  $B=\text{Er}(\text{Co}_{0.988}\text{Ni}_{0.012})_2$ ,  $C=\text{Er}(\text{Co}_{0.975}\text{Ni}_{0.025})_2$ ,  $D=\text{Er}(\text{Co}_{0.965}\text{Ni}_{0.035})_2$ ,  $E=\text{Er}(\text{Co}_{0.95}\text{Ni}_{0.05})_2$ , and  $F=\text{Er}(\text{Co}_{0.925}\text{Ni}_{0.075})_2$  for a magnetic-field variation from 0 to 5 T.

that the isothermal magnetic entropy change exhibits at least the constant value 5 J/Kmol in the range of temperature from 15 K to 36 K. Hence, in this range of temperature this composite material is a good candidate to work as a magnetic refrigerant in the Ericsson cycle.

In conclusion, our theoretical calculations show that both localized spins and itinerant electrons play a key role in the magnetocaloric effect in the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$ . We have also shown that the magnetocaloric effect in the pure intermetallic compound  $\text{ErCo}_2$  is due to two magnetic sublattices, while in the pseudobinary  $\text{Er}(\text{Co}_{1-c}\text{Ni}_c)_2$  the magnetocaloric effect is mainly dominated by only one magnetic sublattice, above a critical Ni concentration. The model presented in this paper is straightforwardly applied to calcu-

late the magnetocaloric effect in other rare-earth cobalt intermetallic compounds such as  $\text{Ho}(\text{Co}_{1-c}\text{Ni}_c)_2$  and  $\text{Ho}(\text{Co}_{1-c}\text{Rh}_c)_2$ . It is also worth pointing out that the present model may be improved by including the degeneracy of the  $3d$  states and the two sublattice character of the compound. However, it is expected that these improvements, which make the numerical calculations much more complex, do not change the main conclusions of this paper.

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