Low-field magnetocaloric effect in Nd2Ni2In intermetallic compound

Efeito magnetocalórico de baixo campo no composto intermetalíco Nd2Ni2In

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ABSTRACT
In this work, we consider a model which describes the CEF and magnetic interaction applied to two sublattices, where the magnetic interaction is described by a Hamiltonian who considers the Zeeman and exchange interactions in the molecular field approximation. The isothermal magnetic entropy change $\Delta S$ as a function of temperature was computationally obtained in the [001] crystallographic direction, from the equation of state of magnetization $M(H, T)$ and entropy $S(H, T)$ by diagonalization of the total Hamiltonian ($H_{Tot}$). We obtained a good agreement between the theory and the experiment was using the estimated crystal-field parameters and the exchange integral for Nd$_2$Ni$_2$In.

Keywords: Magnetocaloric, Antiferromagnetic ordering, intermetallics

RESUMO
Neste trabalho, consideramos um modelo que descreve a CEF e a interação magnética aplicada a dois sublattices, onde a interação magnética é descrita por um Hamiltoniano...
que considera o Zeeman e as interações de troca na aproximação do campo molecular. A mudança de entropia magnética isotérmica \( \Delta S \) em função da temperatura foi obtida computacionalmente na direção cristalográfica [001], a partir da equação de estado de magnetização \( M(H, T) \) e entropia \( S(H, T) \) por diagonalização do Hamiltoniano total (HTot). Obtivemos uma boa concordância entre a teoria e o experimento, utilizando os parâmetros estimados do campo cristalino e a integral de troca para Nd2Ni2In.

**Palavras-chave:** Magnetocalórico, Ordem Antiferromagnética, intermetálicos

1 INTRODUCTION

The magnetocaloric effect (MCE) is an intrinsic magnetic property of each material and can be observed by adiabatic temperature variation \( \Delta T_{ad} \) or isothermal magnetic entropy variation \( \Delta S \) upon variation of the external magnetic field. MCE can be obtained indirectly by magnetization data (MxT or MxH) or through the integration of specific heat data [1]. This effect is more evident around the critical temperature because in this region the magnetization changes faster and consequently there is a greater variation of entropy. In anisotropic materials, the change in the direction of the applied field promotes MCE variation [2,3]. Nd2Ni2In was studied by S. Maskova et.al. 2014, Yu Tyvanchuk et.al. 2012, P. Fischer et al. 2000 among others [4,5]. Nd2Ni2In belong to the family of intermetallic \( R_2T_2X \) (R = Rare-earth, T = transition metal and X = p-metal). This compound crystallizes in the Mo2FeB2 tetragonal structure (P4/mmbm space group) [5].

In Nd2Ni2In present a ferromagnetic interaction along the z-axis with \( T_C \approx 8.5 \) K, and an antiferromagnetic interaction in the basal plane [4,5]. The layered arrangement of the crystal structure leads to large anisotropy and can give rise to geometric frustration. Depending on the type of exchange interaction that occupies its layers. The main objective of this work is to determine the magnetocaloric effect (MCE) of the Nd2Ni2In through of magnetization experimental data [4].

2 THERMODYNAMICS PROPERTIES AND MODEL

In order to investigate the ferromagnetic arrangement MCE, we consider a molecular field model [6,7] where the Hamiltonian for this system is given by

\[
\hat{H}_{TOT} = \hat{H}_{CEF} + \hat{H}_{MAG},
\]

here \( \hat{H}_{CEF} \) represents the crystalline electric field term for a tetragonal symmetry given by
\[ \hat{H}_{CEF} = B_0^0 \hat{O}_0^0 + B_2^0 \hat{O}_4^0 + B_4^0 \hat{O}_6^0 + B_6^0 \hat{O}_8^0 + B_8^0 \hat{O}_{10}^0, \]  

where \( B_n^m \) are the CEF parameters and \( \hat{O}_n^m \) the Steven’s operators. The magnetic term in the molecular field approximation \([8-11]\), is

\[ \hat{H}_{MAG} = -g \left[ (H \alpha_x + \lambda_1 M_{X0}) \hat{j}_x + (H \alpha_y + \lambda_2 M_{Y0}) \hat{j}_y + (H \alpha_z + \lambda_3 M_{Z0}) \hat{j}_z \right] \mu_B \]

here \( g \) is the Landé factor, \( \mu_B \) the Bohr magneton, \( \alpha_x = \cos \alpha_x, \alpha_y = \cos \beta, \alpha_z = \cos \gamma \) are directions cosines for the magnetic field \( H \). \( I = x, y, z \), \( \lambda_1, \lambda_2 \) and, \( \lambda_3 \) are the exchange parameters in the molecular field approximation, \( M_{X0}, M_{Y0}, M_{Z0} \), are the magnetization components, \( \hat{J} = (\hat{J}_x, \hat{J}_y, \hat{J}_z) \) is the total angular momentum operator.

If we denote the eigenvalues and eigenvectors by \( E_j \) and \( |\hat{n}\rangle \) respectively, the magnetization is obtained as

\[ M_I = N g \left( \frac{1}{Z} \sum_{i=1}^{2J+1} (\hat{n}_i |\hat{J}| \hat{n}_i) e^{-\frac{E_i}{k_B T}} \right) \mu_B. \]

where \( Z = \sum_{i=1}^{2J+1} e^{-\frac{E_i}{k_B T}} \) is partition function, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature. The intensity of the magnetization is \( M = \sqrt{(M_x)^2 + (M_y)^2 + (M_z)^2} \) and the total magnetization \( M_{TOT} \) along the magnetic field direction \( M_{TOT} = \alpha_x M_X + \alpha_y M_Y + \alpha_z M_Z \).

The isothermal entropy change can be calculated by the integration of Maxwell relation

\[ \Delta S_{\Delta H} = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \approx \sum_i \sum_k \frac{M_{k+1}(H_i, T_k) - M_k(H_i, T_k)}{T_{k+1} - T_k} \Delta H_k, \]

the last term of Eq.(7) is used in the case of experimental magnetization data.

3 RESULTS

From the experimental data from \( \text{Ni}_2\text{Nd}_2\text{In} \) compound studied by Silvie Maskov [4,5] we obtained the theoretical parameters of the CEF, shown in Table 1, by computational simulations of the theoretical model presented in Eqs. (1-3). A possible magnetic geometrical frustration in \( \text{Nd}_2\text{Ni}_2\text{In} \) motivated by the crystal structure equivalent to the Shastry-Sutherland lattice, suggests an antiferromagnetic arrangement below 0.2 T and above 0.2 T a ferromagnetic order along the c-axis.
Table 1 CEF parameters for Nd$_2$Ni$_2$In compounds obtained from the fit of MxH curves in the [001] direction, the $B_n^m$ are in (K) and $\lambda_{ij}$ in mol·Oe·emu$^{-1}$.

<table>
<thead>
<tr>
<th>Nd$_2$Ni$_2$In [001]</th>
<th>$B_0^2(K)$</th>
<th>$B_0^4(K)$</th>
<th>$B_4^4(K)$</th>
<th>$B_4^6(K)$</th>
<th>$\lambda_{11}$</th>
<th>$\lambda_{12}$</th>
<th>$\lambda_{22}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01888</td>
<td>0.00578</td>
<td>1.0 · 10$^{-8}$</td>
<td>0.00148</td>
<td>4.1119</td>
<td>4.1119</td>
<td>4.1119</td>
</tr>
<tr>
<td></td>
<td>3.7174</td>
<td>3.7174</td>
<td>3.7174</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to simulate the M(H) behaviour using the model discussed above, the following exchange parameters were adopted: below $T_N$, $\lambda_{11} = \lambda_{12} = \lambda_{22} = 4.1119$ mol·Oe·emu$^{-1}$ and above $T_N$ $\lambda_{11} = \lambda_{12} = \lambda_{22} = 3.1774$ mol·Oe·emu$^{-1}$. Fig. 2 shows the magnetic field dependence of magnetization for Nd$_2$Ni$_2$In. The symbols represent the experimental data [4] and the solid curves represent the theoretical calculation. The modulated exchange parameters proposed in this paper, were motivated by the anisotropy of its magnetic arrangements, which in the basal plane is antiferromagnetic and ferromagnetic along the crystallographic direction [001]. The results reveal good adequacy of the experimental data and the theoretical model in [001] crystallographic direction in tetragonal symmetry.

Figure 2: Isothermal magnetic moment M(H). Symbols represent the experimental data and full line the theoretical adjustment.
The CEF energy scheme of the Nd$_2$Ni$_2$In compound was obtained from the diagonalization of the Hamiltonian without the magnetic term. The CEF parameters used to calculate the energy levels shown in Fig. 2 were determined by computational simulations.

The magnetic entropy change $\Delta S_M$ was calculated from $M(H)$ following the common procedure based on Maxwell relations Eq. (5), whereas the $\Delta S_M$ theoretical was obtained with the parameters list in Table 1. The shape of the curves is in accordance with the theoretical results of an antiferromagnetic compound reported by [2, 6].

As we know the set of parameters of CEF is not unique, but the set of parameters of CEF presented in Table 1 were the most adequate to adjusting the isotherms. it is worth mentioning that future measurements realized using neutron scattering will be of great importance in the conformation of this set of CEF parameters. Fig. 3 shows the temperature dependence of $\Delta S$ under magnetic field change from 0 to 1 T for Nd$_2$Ni$_2$In for the same model parameters considered in Fig. 2. The shape of the curves is in accordance with the theoretical results of an ferromagnetic material as reported in refs.[2, 6].
Table 3 Curie temperature $T_C$ or Néel temperature $T_N$, maximum magnetic entropy change under a magnetic-field change of 0–5T for some magnetocaloric materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_N$ or $T_C$ (K)</th>
<th>$\Delta S_{mag}(5\text{T})$ (J/kg K)</th>
<th>Order</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$_2$Ni$_2$In</td>
<td>8.500</td>
<td>3.140</td>
<td>FM</td>
<td>This work</td>
</tr>
<tr>
<td>NdAl$_2$</td>
<td>77.00</td>
<td>0.665</td>
<td>FM</td>
<td>[1]</td>
</tr>
<tr>
<td>DyNiIn</td>
<td>29.00</td>
<td>0.504</td>
<td>FM</td>
<td>[4]</td>
</tr>
<tr>
<td>ErTiSi</td>
<td>46.00</td>
<td>0.08</td>
<td>AF</td>
<td>[5]</td>
</tr>
</tbody>
</table>

These results indicating indicate that from Nd$_2$Ni$_2$In compound magnetocaloric exhibit cryogenics properties superior relative to the others reported in the literature for $\Delta H \sim 0–5T$, therefore, there is applicability potential for “refrigerant device”.

4 CONCLUSION

In this work, we fit $M \times H$ magnetization curves in the [001] direction, obtained by $M \times T$ curves to Nd$_2$Ni$_2$In, with parameters shown in Table 1. From the model we obtained the CEF parameters, the exchange interactions in the molecular field approximation, were obtained, also was estimated $T_C = 8.5$ K as the maximum of the $\Delta S$ curve. Our results are in accordance with the $\Delta S$ curves obtained from the experimental data, and show a good agreement of the proposed CEF and exchange parameters indicated in Table 1. The result in Table 3 indicates the applicability potential of the Nd$_2$Ni$_2$In compound. We also emphasize that the set of CEF parameters pointed may not be unique, and therefore direct measurements of CEF levels by inelastic neutron scattering are extremely valuable to confirm the total Hamiltonian implemented.

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REFERENCES


