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Magnetocaloric effect in Laves-phase rare-earth compounds with the second-order magnetic phase transition: Estimation of the high-field properties

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ABSTRACT

High-field magnetocaloric effect of the rare-earth Laves-phase compounds, which show the second-order magnetic phase transition at low temperatures, has been studied theoretically and experimentally. Both direct and indirect methods are used to characterize the high-field properties of the adiabatic temperature change, ΔT_{ad}, and the magnetic entropy change, ΔS_{mag}, for $TbNi_2$ and $DyNi_2$ compounds, which order ferromagnetically below 37 and 22 K, respectively. Experimental data are compared with theoretical results obtained in the frame of the microscopic model which takes into account the Zeeman exchange interaction and the crystal electric field anisotropy. The high-field magnetocaloric properties near the phase transition are also discussed in the framework of the Landau theory for the second-order phase transitions.

1. Introduction

The magnetic refrigeration which bases on the magnetocaloric effect (MCE) has become an attractive alternative to conventional cooling methods owing to its energy efficiency, ecological safety and possibility of implementation in a wide temperature range [1–3]. Up to now, an intensive search for materials suitable for using as the effective working body of magnetocaloric refrigerators is under way [4–8]. The MCE is intrinsic to all magnetic materials and is due to the coupling of the magnetic sublattice with the magnetic field which changes the magnetic entropy. Thermodynamic quantities that characterize the magnetocaloric properties are the isothermal magnetic entropy change, ΔS_{mag}, and the adiabatic temperature change, ΔT_{ad}, caused by a change of the external magnetic field. These magnetocaloric parameters are usually the highest in the vicinity of a magnetic ordering temperature and decrease progressively beyond the region of the magnetic phase transition. Experimental investigations have shown that materials exhibiting first-order magnetic phase transitions, which possess significantly high ΔS_{mag} and ΔT_{ad} in a narrow temperature range, are attractive for magnetic refrigeration [9,10]. However, apart from these materials, the compounds showing second-order magnetic phase transitions and moderate MCE over a wide temperature range are also of importance, in particular, for the Ericsson-type refrigeration cycle [2].

Several theoretical models can be applied for understanding MCE in ferromagnetically ordered materials [11–14]. For materials with second-order magnetic phase transitions, the magnetic field dependence of MCE near the ordering temperature can be successfully described using the phenomenological Landau's theory

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[15] or a model Hamiltonian [7] which considers the magnetic exchange interaction and the crystal electric field anisotropy. In spite of MCE data obtained in low magnetic fields, both experimental and theoretical results achieved in high magnetic fields are still in demand. In the temperature range from 40 to 300 K, direct investigations of MCE have been performed in fields up to 9 T by Gopal et al. [16]. At lower temperatures, direct studies of MCE in rare earth elements and their solid solutions have been carried out in external magnetic fields up to 6 T by Nikitin et al. [17,18]. However, no results on studies in higher magnetic fields are available. Majority of experiments were performed in fields $\mu_0 H \leq 2$ T, which are relevant for applications [2,19,20]. Restrictions of direct measurements of MCE in higher magnetic fields may result from the complicated experimental technique related to moving thermally insulated sample in and out of the magnetic field [17]. Superconducting magnets traditionally are used for MCE studies in high magnetic fields. Superconducting magnets also work in designing prototypes of magnetic refrigeration construction [21]. The generation of high magnetic fields with a superconducting magnet requires a lot of time and the use of a resistance magnet, for example the Bitter type magnet, seems to be more relevant. For these reasons, experimental setups for direct MCE measurements in high magnetic fields are rather unique. However, extending the field range of the MCE studies could enrich the fundamental knowledge about this phenomenon and reveal new opportunities for applications.

The main purpose of this paper is to identify regularities of the magnetocaloric effect in high magnetic fields. Obtained results are discussed in the frame of both microscopic and phenomenological theories. The model objects for our investigations are $TbNi_2$ and $DyNi_2$ compounds, which order ferromagnetically at low temperatures. These compounds were selected from a great number of intermetallic compounds showing the second-order magnetic phase transition, since their rather simple crystallographic and magnetic structures allow us to perform the reliably theoretical analysis of the experimental results.

2. Theory

2.1. Model hamiltonian and thermodynamic relations

In order to describe magnetic properties and MCE in RNi_2 compounds (R = rare-earth elements), we use the following model Hamiltonian $\mathscr{H} = \mathscr{H}_{el} + \mathscr{H}_{lat} + \mathscr{H}_{mag}$, where $\mathscr{H}_{el} = \sum_k \varepsilon_k c_k^+ c_k$ describes the conduction electrons, $\mathscr{H}_{lat} = \sum_q \hbar\omega_q a_q^+ a_q$ refers to the crystal lattice and $\mathscr{H}_{mag}$ given by

$$\mathscr{H}_{mag} = \sum_{il} \mathscr{J}_0 J_i J_l - g\mu_B \sum_i J_i \mu_0 (H\cos\theta_x + H\cos\theta_y + H\cos\theta_z) + \mathscr{H}_Q + \mathscr{H}_{CEF} \quad (1)$$

describes the 4*f*-localized electrons of rare earth ions [7]. In this magnetic Hamiltonian, the first term describes the interaction between magnetic moments and the second term accounts for the interaction between the magnetic moments and the applied magnetic field, where $\theta_i (i = x, y, z)$ represents the direction along which the magnetic field is applied. The third term describes the quadrupolar interaction [22]. Here we take it in the form $\mathscr{H}_Q = \sum_{il} K Q_i Q_l$, where $Q_i = 3J_{iz}^2 - J_i(J_i+1)$ is the quadrupole moment. The last term accounts for the crystalline electric field. For the cubic symmetry it has the form:

$$\mathscr{H}_{CEF} = W\left[x\frac{\left(O_4^0 + 5O_4^4\right)}{F_4} + (1-|x|)\frac{\left(O_6^0 - 21O_6^4\right)}{F_6}\right], \quad (2)$$

where W is an energy scale and x weights the fourth and sixth order terms [23]. O_m^n are the Steven's operators [24], $F4$ and $F6$ are numerical factors common to all matrix elements [25].

For simplicity reasons we consider the two body interaction terms in the magnetic Hamiltonian in the mean field approximation. The energy eigenvalues (E_i) and eigenvectors are numerically obtained by the diagonalization of the magnetic Hamiltonian. Then, the entropy associated with the magnetic Hamiltonian can be obtained by the thermodynamical relation $S_{mag} = -(\partial F/\partial T)_H$ where $F = -(1/\beta) ln \sum_i e^{-\beta E_i}$ is the free energy, $\beta = 1/k_B T$ and k_B is the Boltzmann constant. Thus, the magnetic entropy is:

$$S_{mag}(T,H,\theta) = \Re\left[ln\sum_i e^{-\beta E_i} + \frac{1}{k_B T}\frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}\right], \quad (3)$$

where $\Re$ is the gas constant. The lattice contribution to the total entropy, considered in the Debye approximation, is given by:

$$S_{lat}(T) = -3\Re ln\left(1 - e^{-\frac{\Theta_D}{T}}\right) + 12\Re\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx, \quad (4)$$

where Θ_D is the Debye temperature. The entropy associated with conduction electrons is $S_{el} = \gamma T$ where γ is the Sommerfeld coefficient. Since the total entropy $S = S_{mag} + S_{lat} + S_{el}$ is obtained, the MCE parameters, ΔS_{mag} and ΔT_{ad}, can be calculated by:

$$\Delta S_{mag}(T, \Delta H, \theta) = S_{mag}(T, H_2, \theta) - S_{mag}(T, H_1, \theta) \quad (5)$$

and

$$\Delta T_{ad}(T, \Delta H, \theta) = T_2 - T_1, \quad (6)$$

under the adiabatic condition $S(T_2, H_2, \theta) = S(T_1, H_1, \theta)$. The model parameters used were: $x = -0.73$, $W = -0.093$meV, $K = 0.05$meV, for $TbNi_2$, and $x = 0.49$, $W = -0.07$meV, $K = 0.001$meV, for $DyNi_2$. These values, chosen to fit the experimental data of magnetization and specific heat, are in the range commonly used in the literature [26–30]. The exchange interaction parameters $\mathscr{J}_0$ were also adjusted to fit the experimental data for the corresponding critical temperature. With these model parameters the magnetocaloric quantities can be calculated for the magnetic field oriented along the crystallographic directions. The magnetocaloric quantities for polycrystalline samples were obtained by taking the weighted average of these quantities.

2.2. Thermodynamic landau theory

Magnetic properties of our samples, with particular emphasis on the field dependence of MCE near the Curie temperature, will be discussed using the Landau theory of the second-ordered phase transitions. According to this theory, the equation for the magnetization of paraprocess near the Curie temperature can be written as [15]:

$$\alpha \cdot M + \beta \cdot M^3 = H \quad (7)$$

were α and β are the thermodynamic Landau coefficients, and M is the magnetization. The expression for MCE caused by an adiabatic