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HoAs: a model compound for the cooling by the barocaloric effect

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Abstract

Recently a novel cooling technique has been introduced based on the barocaloric effect. The effect occurs in rare earth compounds where the crystalline electric field splitting of the rare earth ion can easily be tuned by external pressure or uniaxial stress. As the positions of the low lying crystalline electric field levels have direct influence upon the thermodynamic properties of the system and hence its entropy, adiabatic cooling techniques can be implemented. The monopnictide HoAs shows a barocaloric effect resulting from both a structural as well as a magnetic phase transition. Direct measurements of the barocaloric effect in HoAs and inelastic neutron scattering measurements of the crystalline electric field are presented. The observed barocaloric effect can well be explained by a model taking into account the effects of pressure upon the magnetism as well as upon the structure of the compound.

Keywords: Crystal and ligand fields; Strain; High pressure; Phase transitions; Magnetically ordered materials; Neutron scattering; Diffraction

1. Introduction

Adiabatic cooling techniques are based on a two step process. First, a thermodynamic field is isothermally applied and leads to a reduction of the system's entropy. Second, the field is adiabatically removed and the system is forced to lower its temperature. The most prominent cooling technique of this kind is the well-known adiabatic demagnetization first proposed by Debye (1926) and Giauque (1927), where an external magnetic field leads to the reduction of the spin entropy of the system. In fact it was Warburg (1881) who first observed a change of temperature in iron upon the change of an external magnetic field which is now called the magnetocaloric effect. Progress in the understanding of magnetism and new magnetic materials have lead to a rebirth of this interesting field for possible applications at low temperature and room temperature [1].

Recently, the use of external pressure in order to change the system's magnetic entropy has been proposed and experimentally verified [2–4]. The effect has been called the barocaloric effect (BCE) and occurs in rare earth compounds. The magnetic entropy is given by the level scheme of the crystalline electric field (CEF) split ground state J-multiplet of the rare earth ion

$$S_{\mathrm{m}} = -R\sum_i n_i \ln n_i, \quad n_i = \frac{1}{Z}\,\mathrm{e}^{-E_i/k_{\mathrm{B}}T} \tag{1}$$

where E_i denotes the CEF energy levels, n_i their population factors and Z the partition function. The CEF splitting is of the order of a few $0.1 \ldots 1$ K and governs the thermodynamics at low temperatures. As the CEF splitting results from the electric field of the rare earth ion's neighbors (Stark effect), it reflects its local symmetry and hence is sensitive to any structural change of the compound. Adiabatic cooling by pressure can thus be realized in systems which show a pressure-induced phase transition in close analogy to the adiabatic demagnetization. First, application (or release) of external pressure changes the system's symmetry and leads to a larger CEF splitting and therefore to a lowered magnetic entropy (Eq. (1)). This step has to be done isothermally. Second the system is brought back to its initial state by release (or application) of pressure. If the latter step is done adiabatically the system will lower its temperature. Cooling by a pressure-

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induced structural phase transition has been demonstrated for $Pr_xLa_{1-x}NiO_3$ [2].

Further splitting of the CEF levels can occur by the transition from the paramagnetic into the ordered state (Zeeman effect). Thus, compounds showing pressure-induced magnetic phase transitions can also show a BCE [3,4].

Here we report on direct measurements of the BCE in the monopnictide HoAs, which shows an effect resulting from both a magnetic as well as a structural phase transition. HoAs crystallizes in the cubic rock-salt structure *Fm3m* ($a = 5.771$ Å) and orders below $T_N = 4.3(1)$ K in the antiferromagnetic type-II structure with its moments aligned along the cube edges [5,6]. The Néel temperature is expected to increase under uniaxial pressure. To our knowledge the CEF splitting of HoAs has not yet been investigated by inelastic neutron scattering (INS). As the CEF is crucial for the understanding of the BCE, we have performed INS measurements of the CEF which are shortly presented in the first part of Section 2 followed by direct measurements of the BCE. In Section 3 the results are discussed and a model is given for the quantification of the BCE taking into account both structural as well as magnetic effects in HoAs.

2. Experimental

2.1. Crystalline electric field

The INS measurements of the CEF of HoAs have been performed on the cold triple-axis spectrometers IN12 at ILL, France and DrüchaL at SINQ PSI, Switzerland. Measurements on a single crystal ($3.5 \times 4.4 \times 4.8$ mm^3) were carried out in the paramagnetic state at $T = 10$ K and in the ordered state at $T = 1.5$ K with fixed analyzer energy. Higher order contamination was suppressed by a cooled Be filter after the sample. In the paramagnetic state two unresolved broad shoulders at ± 0.2 and ± 0.4 meV appear with a further peak near 10 meV (Fig. 1). Between 1 and 6 meV no inelastic scattering could be observed. In the ordered state inelastic intensity is observed at 0.8 . . . 1.4 meV and at 1.8 meV. In all these experiments no dispersion of the peaks was found within the experimental accuracy.

The observed data were analyzed by a least-squares fitting procedure (solid line) assuming a Hamiltonian resulting from the cubic CEF interaction and the molecular field (quantized along [001]):

$$\hat{H} = B_4(\hat{O}_4^0 + 5\hat{O}_4^4) + B_6(\hat{O}_6^0 - 21\hat{O}_6^4) - \\ - \lambda_D < \hat{J}_z > \hat{J}_z - \lambda_Q < \hat{O}_2^0 > \hat{O}_2^0 \quad (2)$$

The resulting CEF and molecular field parameters are given in Table 1. The lowest six CEF states are a $\Gamma_3^{(2)}$ ground state doublet, a $\Gamma_4^{(2)}$ triplet at 0.20 meV and a Γ_1 singlet at 0.63 meV (Fig. 3), higher levels are found at 9.8, 10.1, 12.8 and 13.1 meV. The observed intensity around 1.8 meV for $T = 1.5$ K can only be explained by the presence of a quadrupolar field, as the matrix element for this transition would be too weak if dipolar interaction was considered only.

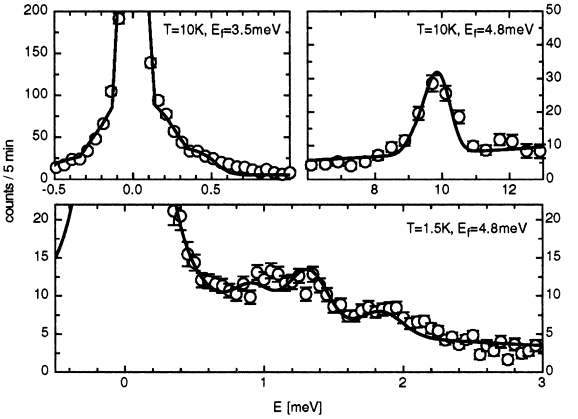

Fig. 1. Energy spectra of HoAs in paramagnetic and ordered state measured on DrüchaL, SINQ PSI (fit with parameters from Table 1).

2.2. Barocaloric effect

For the measurement of the barocaloric effect a cubic crystal of 3 mm side length was placed in a uniaxial pressure device described elsewhere [7] mounted in a standard cryostat, allowing the in situ change of pressure at cryogenic temperatures. Uniaxial pressure was applied along the [001] direction. An Au/Fe-chromel thermocouple was glued on the crystal's surface to track the temperature while applying and releasing pressure. The crystal's support and the piston were made of zirconia to allow almost adiabatic conditions at a sufficiently fast release of pressure. In Fig. 2 we show the barocaloric effect as a function of initial temperature for a pressure release up to 0.3 GPa. The maximal cooling $-\Delta T$ increases almost linearly with pressure and is shifted to higher temperatures *T*. At higher pressures a pronounced shoulder at the high temperature side appears up to around 18 K.

3. Discussion

From measurements on CeSb it is known that the peak position of the BCE can be assigned to the Néel temperature $T_N(p > 0)$ [3,4]. Thus for HoAs a pressure dependence of $dT_N/dp \approx 7.6$ K GPa^{-1} can be estimated from Fig. 2. The broad shoulder at the high temperature side cannot be explained by the phase transition from the ordered to the unordered state as the sample remains in the unordered state at any time.

However the application of uniaxial pressure *p* along

Table 1
CEF parameters for the non-distorted (INS measurement) and the distorted case (calculation based on paramagnetic INS set) [all units in meV]

	t [%]	$B_2^0 \cdot 10^3$	$B_4^0 \cdot 10^4$	$B_4^4 \cdot 10^3$	$B_6^0 \cdot 10^7$	$B_6^4 \cdot 10^6$	$\lambda_D \cdot 10^3$, $\lambda_Q \cdot 10^5$
INS $T = 10\text{K} > T_N$	0		−3.02(5)		−3.87(30)		
INS $T = 1.5\text{K} < T_N$	0		−3.03(5)		−4.66(30)		8.0(1), 3.9(1)
Calculated (BCE)	−0.2	−0.72	−3.03	−1.52	−3.94	8.27	
Calculated (BCE)	−0.3	−1.09	−3.04	−1.52	−3.99	8.35	

[001] leads to a tetragonal distortion. The change in symmetry from *Fm3m* to *I*4/*mmm* alters the splitting of the CEF levels and thus influences the magnetic entropy. Note that in the case of CeSb, the tetragonal distortion does not influence the BCE, as the ground state remains a Kramers doublet and only the excited quartet at 3.2 meV gets split into two doublets, which however has no influence upon the entropy at low temperature.

The distortion in HoAs can be quantified by $t \equiv (c - a)/a = \Delta(c/a)$. With the elastic constants c_{ij} one finds for the limit of cubic symmetry ($|t| << 1$):

$$t = -\frac{c_{11} + 2c_{12}}{c_{11}^2 + c_{11}c_{12} - 2c_{12}^2} \cdot p \tag{3}$$

Using values found in literature for other monopnictides (ErSb, PrSb, YbAs) [8], one gets $t \approx -0.8\%/\text{GPa}$. In tetragonal symmetry five independent CEF parameters have to be considered, as B_2^0 now differs from zero and the relations $B_4^4 = 5B_4^0$ and $B_6^4 = -21B_4^0$ no longer hold. We have estimated the five CEF parameters based on an enhanced point-charge model which also considers the screening due to the conduction electrons of a metal [9] (Table 1). The distortion increases the overall CEF splitting as B_4^0 increases and splits the ground state doublet $\Gamma_3^{(2)}$ into two separate singlet states and the triplet state $\Gamma_4^{(2)}$ into a singlet and a doublet. The resulting magnetic entropy (Eq. (1)) is significantly reduced and hence explains the BCE above the Néel point (Fig. 3). In order to model the BCE below T_N we have performed mean-field calculations based on the Hamiltonian of Eq. (2) (Fig. 3). As the molecular field parameters λ_D and λ_Q are only known from INS for the non-distorted case, they were adjusted by matching the experimentally observed pressure dependence of T_N. Based on these assumptions the BCE $-\Delta T$ was calculated by solving the adiabatic equation

$$S(p = 0, T + \Delta T) = S(p > 0, T) \tag{4}$$

for the system's total entropy $S(p,T) = S_m(p,T) + S_{latt}(p,T) + S_{e^-}(p,T)$ including phononic and electronic contributions, too. The phononic part was modelled by the Debye function using $\Theta_D = 230$ K extrapolated from non-magnetic LaAs and LuAs [10]. The electronic contribution was assumed to be linear at low temperatures with $S_{e^-} = \gamma \cdot T$ and $\gamma \approx 10\ \text{mJ K}^{-1}\,\text{mol}^{-1}$. Both contributions are only weakly pressure dependent (the elastic heating due to the change in S_{latt} is less than ≈ 10 mK at 5 K and 0.5 GPa in YbAs [11]). Fig. 2 shows the best fit, which well explains the shape of the BCE – except close to the magnetic phase transition temperature, where fluctuation phenomena must be considered too. The observed values of the BCE are a factor four less than the calculated values (i.e. in Fig. 2 the calculation has been downscaled by 0.25 to fit the observed data). However it has to be kept in mind that the sample could not be perfectly isolated from its environment. The release of pressure has to be assumed not being fully adiabatic, as heat leakage through the socket and the piston must be expected. The heat transfer through the thermocouple can only be decreased by minimizing the sensor but remains inherently a problem of any measurement of an adiabatic process.

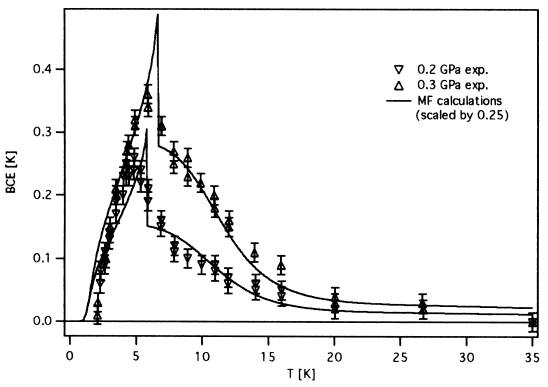

Fig. 2. Measured BCE together with a model calculation (CEF parameters from Table 1, $T_N = 5.9$, 6.7 K, $\lambda_D = 19.3$, 20.5 μeV, $\lambda_Q \equiv 20$ neV for the 0.2 and 0.3 GPa data set, respectively).

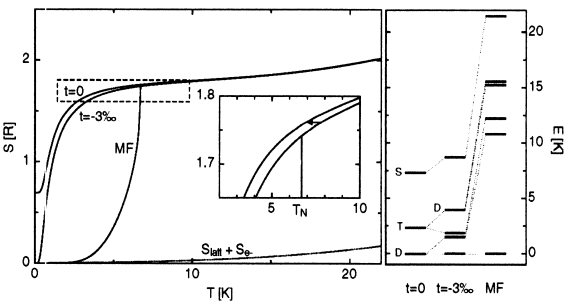

Fig. 3. Calculated total entropies and level schemes of the six lowest energy levels for the non-distorted, distorted and Zeeman split case (dashed: non-magnetic entropy). Due to the distortion cooling above T_N is possible (arrow in inset). The non-distorted and Zeeman split level schemes correspond to the INS measurements at $T = 10$ and 1.5 K, respectively.

4. Summary

An example of a compound showing the barocaloric effect (BCE) has been given. The effects contributing to the BCE could be implemented by a model based on microscopic properties of the material. Magnetic and structural phase transitions are simultaneously responsible for the observed cooling. The understanding of the BCE eases the way to find other candidates suited for cooling by the BCE.

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