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A novel principle for cooling by adiabatic pressure application in rare-earth compounds

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Abstract

A novel principle for cooling by adiabatic pressure application in rare-earth compounds is introduced. The principle is based on the occurrence of a pressure-induced structural and/or magnetic phase transition where the point symmetry at the rare-earth site is changed involving a change of the degeneracy of the crystal-field ground state and/or a complete lifting of the degeneracy of the crystal-field states by the Zeeman effect. Cooling can then be achieved under adiabatic application (or removal) of pressure as will be demonstrated for the rare-earth compounds $Pr_{1-x}La_xNiO_3$ and CeSb. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Upon removal of a magnetic field from a material, the resulting reduction in magnetic spin alignment represents an increase in the material's spin entropy. If the field reduction is performed adiabatically, there will be a decrease in the temperature of the material which is called the magnetocaloric effect. Cooling rates of typically 1 K per 1 T field change have been achieved so far, with a maximum of about 4 K predicted for $Gd_5(Si_xGe_{1-x})$ which is called the ''giant'' magnetocaloric effect [1]. Recently, we introduced a novel principle for cooling based on adiabatic pressure application on the rare-earth nickelate compound $Pr_{1-x}La_xNiO_3$ [2], i.e. cooling by the well-known magnetocaloric effect is replaced by the barocaloric effect. A cooling effect of 0.1 K per 0.5 GPa hydrostatic pressure change was achieved for a polycrystalline sample of $Pr_{0.66}La_{0.34}NiO_3$ at a working temperature around 350 K [3]. Cooling is more efficient for single crystals and uniaxial pressure. This was verified for the rare-earth compound CeSb at a working temperature around 20 K. We found a ''giant'' cooling rate of 2 K per 0.52 GPa pressure change which opens the way to technical cooling systems without the application of high magnetic fields and the presence of liquified gases used in conventional adiabatic demagnetization and adiabatic expansion techniques, respectively.

2. The barocaloric effect in $Pr_{1-x}La_xNiO_3$

We employed neutron diffraction and spectroscopy as well as magnetic susceptibility and heat capacity measurements to characterize the physical properties of the compounds $Pr_{1-x}La_xNiO_3$ which undergo a structural phase transition (SPT) from a high-temperature $R\bar{3}c$ rhombohedral to a low-temperature orthorhombic Pbnm phase in the concentration range $0 \leq x < 0.7$ [4–6]. The SPT turns out to be very broad, i.e. the two phases co-exist in a temperature range of about 100 K. The application of hydrostatic pressure shifts T_{SPT} typically by $dT_{STP}/dp \approx -5$ K/kbar. This means that external pressure modifies the sample such that the volume fraction of rhombohedral symmetry is enhanced at the expense of the orthorhombic component. The crystalline-electric-field (CEF) ground state is a singlet in the Pbnm phase, whereas a non-Kramers doublet is the lowest crystal-field state in the $R\bar{3}c$ phase [5]. The entropies of the two phases differ by $\Delta S \approx 5.5$ J/mol K, which enables cooling by adiabatic pressure application as described in detail in Ref. [3].

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We studied the barocaloric effect for polycrystalline $Pr_{1-x}La_xNiO_3$ with $x = 0.34$ [3] and more recently for $x = 0.5$ and 0.6 [6]. For $x = 0.34$ we found a tiny cooling effect of 0.1 K per 0.5 GPa pressure change at a working temperature around 350 K, but practically no cooling for $x = 0.5$ and $x = 0.6$ at working temperatures around 180 and 50 K, respectively. This is due to the fact that the expected cooling was largely compensated by the competing effects of pressure-induced elastic heating and friction, the latter being a particular problem in experiments on polycrystalline samples. We therefore conclude that efficient cooling can only be achieved by using ceramic or single-crystalline material. Moreover, efficient cooling is restricted to low temperatures, since the entropy of the phonons dominates the CEF entropy at temperatures above say 30 K.

3. The barocaloric effect in CeSb

The rare-earth compound CeSb has been thoroughly studied in the past because of its fascinating magnetic phase diagram. CeSb crystallizes in the cubic NaCl structure. Below $T_N \approx 16$ K antiferromagnetic ordering occurs in various phases which are all characterized by a periodic stacking of ferromagnetic (001) layers with up or down magnetization and nonmagnetic layers, giving rise to characteristic ordering wave vectors $\boldsymbol{q}_0 = (2\pi/a) \times (0,0,q_0)$ with $1/2 \leq q_0 \leq 2/3$ [7,8]. The onset of magnetic ordering is accompanied by a structural phase transition from cubic to tetragonal symmetry [9]. The tetragonal state can also be realized by the application of uniaxial pressure along the [001] axis. As a result the magnetically ordered state can be reached for temperatures $T > T_N$, with $dT_N/dp \approx 8$ K/GPa [10] as visualized in the p–T phase diagram of Fig. 1.

The Ce^{3+} ions in CeSb experience the CEF interaction which splits the lowest J-multiplet of the Ce^{3+} ions into a ground-state doublet and an excited quartet [11]. The CEF splitting is about 3 meV. The cubic-to-tetragonal phase transition induced by uniaxial pressure splits the quartet into two doublets which lowers the entropy of the system. This is the basis for cooling by adiabatic (de)pressurization [2,3]. The entropy decrease is further enhanced by the onset of magnetic ordering below T_N due to a complete lifting of the degeneracy of the CEF states through the Zeeman effect, thereby amplifying the barocaloric effect substantially. Fig. 2 shows schematically the evolution of the entropy as a function of temperature and pressure. The key element is the discontinuity of the entropy at T_N which was determined by heat capacity measurements to be $\Delta S \approx 2$ J/mol K [6], comparable to the refrigerant capacity reported for the ‘‘giant’’ magnetocaloric effect [1].

Let us now assume that the system is in the paramagnetic state at a temperature $T > T_N$, say at point A in Figs. 1 and 2. We now perform the process of isothermal pressurization such that the system transforms into the magnetically ordered state, thereby moving vertically to point B. For the next step the sample has to be isolated from its surroundings, so that the process is adiabatic. The sample is depressurized and moves horizontally to point C as shown in Fig. 2. This process is the barocaloric effect which lowers the temperature of the system. It is clear from Fig. 2 that the cooling increases (linearly) with increasing pressure, and the maximum cooling corresponds to the pressure-induced temperature shift of the discontinuity of the entropy curves, i.e. $\Delta T_{max} = T_N(p = 0) - T_N(p > 0)$. The latter expression holds for reasonably moderate pressures up to about 1 GPa.

We performed barocaloric experiments on a CeSb single crystal of volume $2.7 \times 2.3 \times 2.1$ mm^3. The crystal with nice ⟨001⟩ cleavage planes was mounted in a uniaxial pressure device described elsewhere [12]. The pressure is generated in a hydraulic cylinder and transmitted through a plunger onto the single crystal mounted between two 0.1

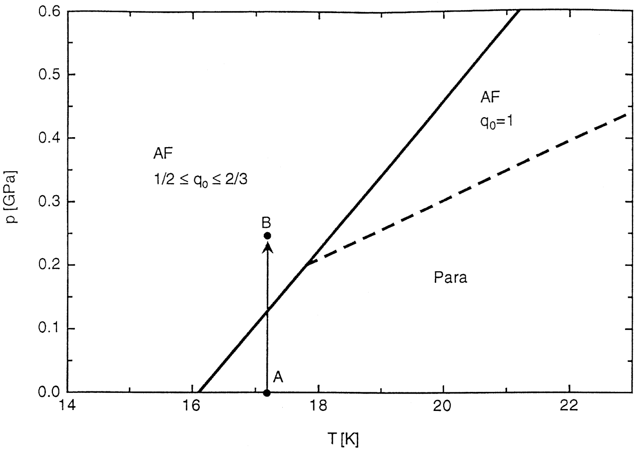

Fig. 1. Magnetic phase diagram of CeSb (after Ref. [10]). The full and broken lines denote first-order and second-order phase transitions, respectively.

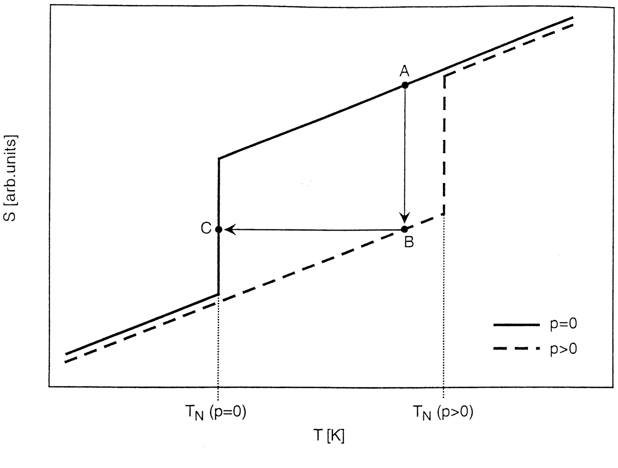

Fig. 2. Schematic plot of the temperature and pressure dependence of the entropy for CeSb.

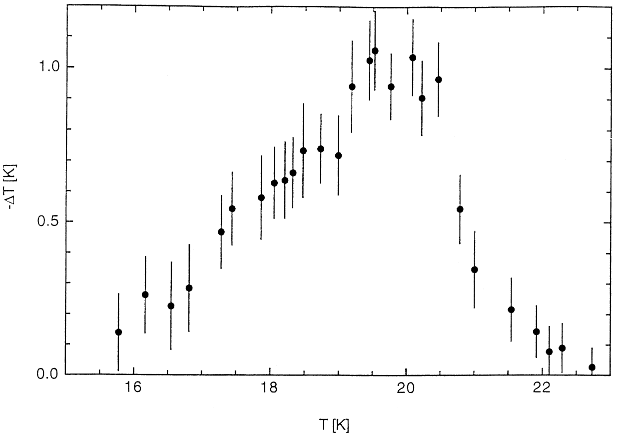

Fig. 3. The barocaloric effect ΔT observed in CeSb upon releasing a uniaxial pressure of 0.26 GPa.

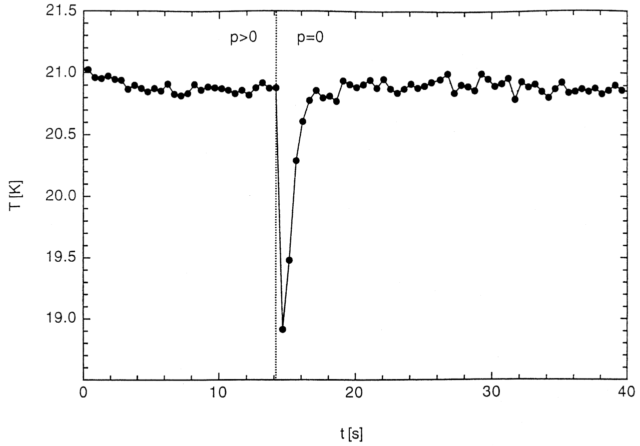

Fig. 4. Time dependence of the sample temperature in CeSb upon releasing a uniaxial pressure of 0.52 GPa.

mm thin Teflon foils in a He cryostat. An essential feature of the experimental setup is the in situ measurement of the sample temperature. This was achieved by means of an alumel–chromel thermocouple device optimized for low-temperature measurements [6]. The results obtained for $p = 0.26$ GPa are shown in Fig. 3. The temperature evolution of the cooling rate nicely follows the theoretical predictions outlined in Fig. 2. Efficient cooling ΔT is achieved in the temperature interval $16 < T < 21$ K. The cooling increases linearly upon raising the initial sample temperature, until a maximum cooling of $\Delta T \approx -1$ K is achieved. Above about 20 K the cooling effect breaks down rapidly, since the applied pressure is too small to induce the magnetic phase transition. A marginal cooling of the order of -0.1 K is observed above 21 K and below 16 K due to the release of the elastic energy, which can readily be understood from Fig. 2. So far a maximum cooling effect of $\Delta T \approx -2$ K has been observed for $p = 0.52$ GPa at an initial sample temperature of 21 K as shown in Fig. 4.

4. Concluding remarks

The maximum cooling rate observed for CeSb is likely to be increased significantly by properly optimizing the experimental setup. As can be seen from Fig. 2, the adiabatic cooling step B→C is expected to end at $T_N(p = 0) \approx 16$ K as the lowest possible temperature limit which was not reached in the present experiments. This is related to several factors such as inertia of the thermocouple, heat transport through the thermocouple and, most importantly, insufficient thermal isolation of the sample, i.e. our observation of the barocaloric effect was not an ideal adiabatic process as manifested in Fig. 4 due to the rapid temperature relaxation after the pressure release. In future measurements this experimental insufficiency will be largely removed by transmitting the pressure through isolating anvils (e.g., made of zirconium oxide).

Finally, it is worth mentioning that the barocaloric effect in CeSb is not restricted to the small temperature range above $T_N \approx 16$ K. By partial substitution of Ce^{3+} ions by non-magnetic Y^{3+} or La^{3+} ions the magnetic ordering temperature is shifted downwards, typically by 5 K per 10% Y or La substitution [13] which opens the way to cooling to the technically interesting milli-Kelvin range. Indeed, we have verified the lowering of T_N upon dilution by neutron diffraction experiments on a single crystal of $Ce_{0.85}(La_{0.95}Y_{0.05})_{0.15}Sb$ which shows the onset of short-range magnetic correlations below 7.8 K. By the application of uniaxial pressure ($p > 0.1$ GPa) the magnetic fluctuations are found to develop long-range magnetic ordering. The critical temperature is raised at rate $dT_N/dp \approx 13$ K/GPa, which is considerably larger than for undiluted CeSb and therefore highly beneficial for the efficiency of the barocaloric effect.

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