UNIVERSITA' DEGLI STUDI DI PARMA

Dipartimento di Fisica e Scienze della Terra

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Report on the doctoral Thesis
RNDr. **Jiří Kaštil**
Magnetocaloric properties of rare-earth compounds

This doctoral thesis reports on a theme of experimental physics of condensed matter, that is, the magnetocaloric effect (MCE) of systems characterized by a peculiar magnetic behaviour. In particular, the studied systems were rare-earth based intermetallic compounds and Heusler alloys, with a different degree of crystalline order. Several samples have been prepared and thoroughly characterized by the point of view of their structure, chemical composition, resistivity, magnetic and thermodynamic properties. A particular mention has to be given to the design and set-up of an innovative technique for the direct measurement of the temperature variation occurring in consequence of the magnetocaloric effect. This experimental activity, performed in collaboration with the Institute of Physics ASCR, v. v. i. (FZU), constitutes a central point in this thesis, in that it has allowed the obtainment of interesting results required for a complete characterization of MCE in the studied systems. Moreover, the data obtained by this method enabled the discovery of the applicative potential of measured effect. Although it can be categorised as basic research, this work has indeed an implicit horizon linked to a potential technological application in the field of magnetic refrigeration.
From the point of view of fundamental physics of condensed matter, the research activity performed in the framework of this doctoral thesis has covered the issues of magnetic properties of solids, in particular concerning the magneto-crystalline anisotropy, and of phase transitions, in correspondence of which the MCE is better developed.
This thesis is organized on five chapters. After a brief introduction highlighting the aim of the work, a chapter is devoted to the theoretical background that includes an overview of the magnetic properties of condensed matter and of phase transitions and a presentation of the magnetocaloric effect. The third section describes the experimental methods used, with particular emphasis on the developed technique for the direct measurement of MCE. The main part of the thesis (chapter four) represents then the achieved results and their discussion and finally main conclusions are given in chapter five. The structure of the thesis is appropriate and the general readability and clarity is good, although the text is affected by some language shortcomings.
An important result that has been obtained concerns the influence of magneto-crystalline anisotropy on the MCE in a single crystal of TbNiAl, as compared to polycrystalline samples. Moreover, the controlled introduction of a partial degree of disorder by suitable substitutions of TbFeAl and GdFeAl has been proven to cause a spreading of the temperature range on which a useful MCE is shown. The same effect results in the case of amorphous metallic GdCoAlY alloys, characterized by a high degree of disorder. In the case of NiMnGa-based Heusler alloys, some interesting results have been obtained as regards the influence of pressure and of Er conditioning on the inverse MCE behaviour in the closeness of the magneto-structural transition. All the obtained results can be considered as original and the publication of the most relevant ones on international Journals (Refs. 39, 47, 57, 59) witnesses their relevance in the area of physics of condensed matter. It has to be noted that the results reported in this thesis can find possible application to other areas, like as materials science and engineering of energy conversion.
The main points of force of this work are:

- The realization of an innovative method for the direct determination of the adiabatic temperature change;
- A thorough characterization of rare-earth based compounds with a different degree of order.

The main weakness is the lack of a comprehensive view of the remarkable mass of experimental results obtained for the rare-earth based compounds, in the attempt to trace some general correlation between the magnetocaloric behaviour and the degree of crystalline order.

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I have some minor remarks and questions relative to specific points:

1. The part treating the possible use of Maxwell's relation to deduce the entropy change from magnetization measurements in the case of a first-order process [p. 18] does not mention the need of using a proper measurement protocol to avoid a partial phase transformation (L. Caron, et al., J. Magn. Magn. Mater. 321 (2009) 3559). Which protocol have you utilized during magnetization measurements of samples with a first-order hysteretic transition?
2. The sentence "A change of the sample temperature induced by MCE is instantaneous (comparable with spin relaxation time, $\tau \sim 10^{-6}$s) in whole volume of sample" [p. 39] deserves a deeper discussion. Could you comment, on the basis of your results, about how the specific nature of the transition (first-order, martensitic diffusionless, …) and/or the degree of order of the sample (polycrystalline, with structural and/or compositional inhomogeneity, ...) could affect MCE dynamics?
3. [p. 32-39] A discussion on the uncertainty related to the results of the proposed technique for the measurement of adiabatic temperature change is lacking. Could you estimate the expected error after the individuation of the possible error sources?
4. "The absolute values of magnetization (Fig. 4.11) are unfortunately subjected to considerable error due to extremely small sample dimension and weight. However, the obtained pressure dependences are nevertheless valid." [p. 51] The propagation of this large error on calculating the entropy changes represents a non-negligible factor that could affect the validity of the obtained pressure dependences: for example, the results shown in fig. 4.12 and 4.13 could correspond in some cases to a negligible pressure dependence, if the error bars would be larger than data spread. Similarly, the whole discussion on the dependence of entropy change from the Y content [p.54-55] should be related to the level of uncertainty in the determination of ΔS (and of RCP).
5. The proposed explanation for the different results of direct measurement of temperature change obtained in this work and in literature [p. 76] is not convincing. In fact, it is based on the relation between a supposed dynamics of the magneto-structural transition, which has not been clarified (question 2), and the measurement times. Moreover, the comparison of results obtained on different samples by different techniques should be considered only very carefully (K. Morrison, et al., Int. J. Refrig. 35 (2012) 1528), even if the stoichiometry is similar.
6. "Unfortunately, the direct measurements of ΔT_{ad} of the very flat shaped samples were strongly stigmatized by two effects – by significant thermal losses from such samples during the measurement of ΔT_{ad} and probably also by a sharp set-out of temperature around colder (or warmer) thermocouple due to a low thermal conductivity of the metallic glass." [p.95] Could you discuss this point in more detail, as it represents a limitation of the proposed technique for the direct measurements of ΔT_{ad}?

As conclusion, the presented work clearly demonstrates the ability of Jiří Kaštil to perform creative scientific work and I recommend acknowledging this work as a successful PhD Thesis.

Parma, September 8, 2014

Prof. Massimo Solzi