Referee report on the PhD thesis of Mgr. Yuriy Skorokhod

"Pressure effects on the magnetocaloric $R_5(Si_xGe_{1-x})_4$ compounds"

Magnetocaloric effect is known for a long time but in recent decade it attracted a "fresh" attention after the applicability of this effect to real magnetic refrigerators at room temperature was shown on Gd. Extensive world-wide search for more convenient (from several viewpoints) refrigeration materials led to a great attention to rare-earth intermetallic compounds R_5M_4 (M = Si, Ge) and their solid solutions in which a magnetic transition occurs together with structural transition, and both the transitions are strongly coupled. Thus, a change of the magnetic state induced by external magnetic field leads to structural transition which becomes field-controlled. Involvement of the structural transition increases considerably the magnetocaloric effect.

It is natural that the transitions are accompanied by large changes in interatomic distances and should be sensitive to external or "chemical" pressure. The thesis of Yuriy Skorokhod is devoted to a detailed study of magnetoelasticity of several representatives of R_5M_4. It presents results of the hydrostatic pressure effects on the magnetic, magnetoelastic and magnetocaloric properties of Gd_5Ge_4, $Gd_5Si_{0.4}Ge_{3.6}$, $Tb_5Si_2Ge_2$, $Nd_5Si_{1.45}Ge_{2.55}$ and $Pr_5Si_{1.5}Ge_{2.5}$. The work was done in close collaboration with research group of University of Saragossa where all the sample have been prepared.

The thesis consists of 105 pages and is divided in 6 chapters plus List of references, Acknowledgements and List of publications. It contains 76 figures, 4 tables and 72 references. After introduction (Chapter 1), the author gives a theoretical background (Chapter 2) of the phenomena considered in the original part of the thesis. The chapter provides an adequate introduction for further interpretation of the observed results. The experimental techniques and details of measurements are described in Chapter 3. State of art in knowledge about structure, magnetism and magnetocaloric effect in R_5M_4 compounds is presented in Chapter 4. The main part of the thesis is formed by Chapter 5, containing the original results. General conclusions are summarized in the Chapter 6. The thesis is written in good English.

As the most interesting obtained results I would like to mention the observed pressure-induced ferromagnetism in Gd_5Ge_4 and enhancement of the magnetocaloric effect in $Tb_5Si_2Ge_2$ by external pressure. Both these results are published in Phys. Rev. Letters.

After critical reading of the thesis, I have several remarks and questions to the author.

1. "Monoclinicity". The monoclinic structure observed in the studied compounds as an intermediate stage between two orthorhombic structures is rather important for understanding of the obtained results. However, it is not properly described in the thesis either in description of the crystal structures (Chapter 4) or in the original part. Moreover, I did not find any characteristics of "monoclinicity", only lattice parameters a, b, a are presented for monoclinic representatives. Which angle deviates from 90 degrees and how strong is the monoclinic distortion?

2. Fig. 4.8 shows a zero-field phase diagram of $Gd_5(Si_xGe_{1-x})_4$. From this diagram, compound with x = 0 (Gd_5Ge_4) is ferromagnetic with T_C about 20 K. I think, I would be good to mentioned already here that it is not correct, as is shown in the Chapter 5, "the ferromagnetic order was not observed in Gd_5Ge_4 in zero magnetic field down to the lowest measured temperatures" and is field-induced (or pressure-induced, as is observed by the author).

3. The unit system CGS is used in the thesis (kOe, emu/g, kbar). However, when the author presents the thermodynamic properties (specific heat and entropy) he uses J $kg^{-1}K^{-1}$, i.e. SI units. Mixture of systems within one work is not so good.

I have found in the thesis few misprints and other minor errors but their number does not exceed an acceptable level.

In conclusion, the work represents an extensive experimental study with many interesting results and their proper interpretation. I think that the author, Yuriy Skorokhod, satisfies the requirements of the PhD degree.

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