23.06.2023

Influence of hydrostatic and chemical pressure, and magnetic field on caloric phenomena in pure and doped Fe_7Se_8 single crystals

This thesis is devoted to investigations of magnetic properties, magnetocaloric (MCE) and barocaloric (BCE) effects in pure and doped single crystals of Fe_7Se_8 (3*c* type). Innovative cooling solutions that do not rely on ecologically damaging refrigerants and can offer a greater energy-efficiency than the traditional vapor-compression technique are in demand due to the need for cooling equipment and the accompanying energy expenses. It is the reason why magnetocaloric cooling attract attention of researchers from the material and fundamental sciences, as well as engineers. The main aim of the studies was to determine and to understand the effect of replacing iron with nickel and cobalt on the structure, magnetic and magnetocaloric properties of $Fe_{7-x}Ni_xSe_8$ and $Fe_{7-x}Co_xSe_8$ single crystals (hexagonal NiAs-like structure) and to compare it with the effect of hydrostatic pressure. In order to check the mechanisms responsible for the observed effects, an attempt was made to determine the correlation between the MCE and magnetostriction. Measurements have been carried out in a magnetic field up to 10 T over the temperature range from 2 to 490 K.

Here is presented the analyse of the influence of Co and Ni ion doping on the crystal structure, phase transitions, and magnetic properties of the Fe_7Se_8 system for composition range: $(Fe_{0.987}Ni_{0.013})_7Se_8$, $(Fe_{0.955}Ni_{0.045})_7Se_8$, $(Fe_{0.915}Ni_{0.085})_7Se_8$, $(Fe_{0.89}Ni_{0.11})_7Se_8$, $(Fe_{0.79}Ni_{0.21})_7Se_8$, $(Fe_{0.975}Co_{0.025})_7Se_8$, $(Fe_{0.951}Co_{0.049})_7Se_8$ and $(Fe_{0.91}Co_{0.09})_7Se_8$ and the parent material Fe_7Se_8. Because the ionic radii of doping ions are smaller than those of Fe^{2+} ions (responsible for magnetic properties of Fe_7Se_8 crystals), the substitution effect causes a systematic reduction in the unit-cell volume, affects the magnetic subsystem and determine the magnetic ordering temperature T_C and the spin-reorientation temperature (T_{SRT}). The most important result of this thesis was the demonstration of the substantial correlation between hydrostatic and chemical pressures in the studied systems. The nature of magnetic phase transitions has been characterized in the vicinity of T_C and T_{SRT}, the magnetic entropy change (ΔS_m) and refrigeration potential magnitudes have been established for this temperature range. The substantial dependence of these parameters on chemical and hydrostatic pressure has been demonstrated. It was found that a systematic change in the unit cell constants, induced by an external magnetic field, strongly correlates with the change in the T_{SRT} and the magnetic entropy change. The data suggests that the connection between magnetostriction and the MCE, reported previously for different materials, is universal, and magnetostriction can be used to predict the ΔS_m in Fe_7Se_8 single crystals doped with transition metals. Based on experimental results, a phenomenological model was developed, and it was shown that the hydrostatic pressure, the ratio of the quantity of Fe^{2+} and Fe^{3+} ions, and the crystal field acting on Fe^{2+} ions all had a significant impact on the system's magnetic properties.

Yaroslav Konopelnyk