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Resonant photoemission study of MnFePAs compounds exhibiting giant magnetocaloric effect

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Magnetic refrigeration which is based on the magnetocaloric effect (MCE) has emerged as a serious alternative to conventional refrigeration. Recently, the group of compounds $(Mn,Fe)_2P_{1-x}As_x$ has been found to exhibit the giant magnetocaloric effect which is related to the first-order phase transition, and is tunable around room temperature [1]. The P/As ratio appeared to be an interesting method to tune the basic properties for any application such as Curie temperature and thermal hysteresis width [2]. In order to understand the effect of substitution we performed the extended studies of the electronic structure, crystal structure and magnetism for the selected group of solid compounds $Mn_{1.1}Fe_{0.9}P_{1-x}As_x$ ($0.4<x<0.55$). The substitution of silicon by arsenic has strong influence on the value of the magnetocaloric effect and the phase transition temperature. Despite the standard method of determination of the magnetic entropy changes from the magnetic measurements in conjunction with the Maxwell relations we measured the direct adiabatic temperature change which reached the high value of 4 K at the field of 1.7 T for x=0.5 and Si substituted by As [3].

The main goal of our work was finding the relationship between magnetic properties and electronic structure of magnetocaloric materials, and their comparison with the results of theoretical calculations. In order to determine the electronic structure of manganese combined with their magnetic properties we have performed detailed x-ray resonant photoemission (RESPE)) studies on Mn $L_{2,3}$ edge and Mn M edge and x-ray magnetic circular dichroism (XMCD) studies under an applied magnetic field of 0.47 Tesla for $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.4}Si_{0.1}$ and $Mn_{1.1}Fe_{0.9}P_{0.6}As_{0.4}$ samples prepared by SPS (spark plasma sintering) method.

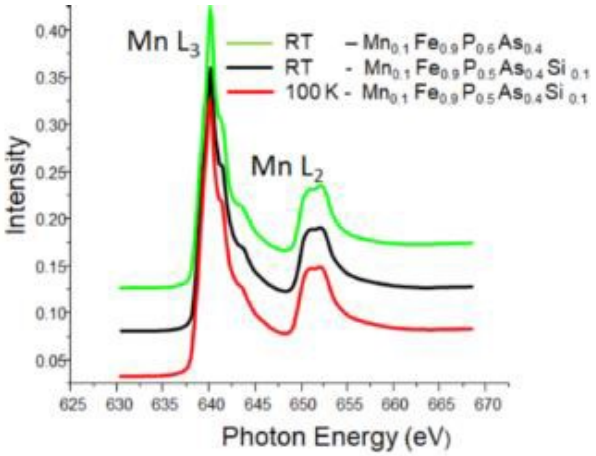

Figure 1. Mn L-edge XAS spectra obtained for reference sample and with Si substitution recorded at room temperature and T=100K.

The general shape of the Mn-L edge of studied samples can be described by strong peak with additional two features within the shape of L_3 edge and at least two components within L_2 edge (see Fig. 1). The resonant photoemission studies performed for particular points of absorption spectra measure both for L-edge and M-edge showed participation of 3d manganese states in the valence band. The clear exchange splitting effect have been on core level Mn2p have been observed at low temperature. Further, we detected a small XMCD signal on Mn L edge at 100 K (see Fig. 2), thus providing a direct evidence of the especially role of Mn atoms in magnetic properties of MnFePAs series.

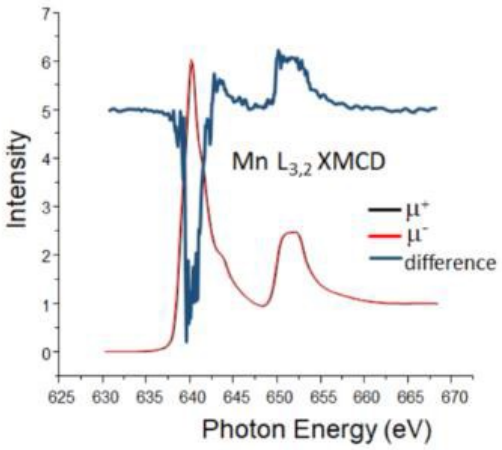

Figure 2. X-ray absorption spectra for $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.4}Si_{0.1}$ compound. Gently difference between shape of the curves can be found and difference spectrum is also shown.

Additionally we performed the analysis of the influence of silicon on the partially density of states of manganese and iron of the $Mn_{1.1}Fe_{0.9}P_{1-x}(As,Si)_x$ system. We found a differences in the electronic structure of the iron and manganese elements located two different positions 2f and 2g in the elementary cell, respectively. The obtained results indicated the impact of silicon substitution on the changes of adiabatic temperature change in relation to the observed changes in the magnetic moment of manganese in range of phase transition.

References

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