Magnetocaloric materials and first order phase transitions

This thesis studies the first order phase transitions of the magnetocaloric materials La$_0.67$Ca$_{0.33}$MnO$_3$ and La(Fe,Mn,Si)$_{13}$H$_{x}$, trying to overcome challenges that these materials face when applied in active magnetic regenerators. The study is done through experimental characterization and modelling of the properties of such materials. The experimental characterization of these materials is done through various different methods, such as X-ray diffraction, magnetometry, calorimetry, direct measurements of entropy change, capacitance dilatometry, scanning electron microscopy, energy-dispersive X-ray spectrometry and magnetocaloric regenerative tests. The magnetic, thermal and structural properties obtained from such measurements are then evaluated through different models, i.e. the Curie-Weiss law, the Bean-Rodbell model, the free electron model and the Debye model. The measured magnetocaloric properties of La$_0.67$Ca$_{0.33}$MnO$_3$ shows a paradoxical behavior; the material shows features of both a first order phase transition and of a second order one. Identities as shift of the heat capacity peak and an asymmetric growth of of the entropy change with magnetic field would describe this material transition as a first order one. However, the material did not present any signs of intrinsic hysteresis, a feature common in first order transitions. This is attributed to a chemical distribution in this first order phase transition material that can lead to a smearing of the transition and the hysteresis, and such effect is observed through modelling. Moreover, inverse susceptibility measurements showed what could be evidences of magnetic polarons being formed in the paramagnetic phase of the material. The origin of the first order transition seems to be due to the magnetoelectric coupling observed through isothermal magnetostriction and dilatometric measurements. Although the Bean-Rodbell model has described with a good agreement the entropy change, hysteresis, magnetization and heat capacity, it has failed to describe the isothermal magnetostriction. It is suggested that such failure could be related to different factors that might influence constructively to each other: (i) the model assumes localized magnetic moments, while this material presents a double exchange interaction; (ii) the model assumes a temperature and field independent bulk modulus, which literature has shown that is not the case; and (iii) the approximation of the cluster being temperature and field independent is exaggerated and perhaps cannot be taken. A series of La(Fe,Mn,Sn)$_{13}$H$_{x}$, with slightly changes in the composition is also evaluated here. This material may present a second order phase transition for large content of Mn and Sn, which will become a first order one as the Mn and Sn content decreases. The material also presents a volume change, which also increases as Mn and Sn content decreases, which in return may lead to detrimental mechanical stability of the material during application. The shift of the orderliness from second to first order transition is observed through heat capacity, magnetization and entropy change measurements. By measuring bulky particles (with a particle size in the range of 500-1000 μm) of La(Fe,Mn,Sn)$_{13}$H$_{x}$ with first order phase transition, it was possible to observe very sharp transitions. This is not the case for finer ground particles which show a smooth transition, as if it was second order. Although this behavior has been explained in the literature as an artefact due to the inclusion of defects when grinding the material, here it is proposed a different explanation given the evidences. Firstly, it is argued that the material is brittle and insertion of defects through grinding is unlikely. Secondly, it is observed through entropy change measurements that a bulky particle has a larger entropy change. However, the particle cracks and separates into several particles due to stresses generated during the transition, which are related to the volume change. After this effect, if the entropy change is remeasured it shows very similar behavior to measurements of ground particles. Therefore, the results suggests that defects inserted through grinding is probably not the case. To explain such behavior, in this thesis it is proposed that slightly differences in the composition throughout the sample may lead to a Curie temperature distribution. This in return would lead to different regions of the sample undergoing the transition in different temperatures. However, given the polycrystallinity of the material, the crystallites with different Curie temperatures will be volumetric constrained until enough energy is given to the system and the whole bulky particle undergoes the transition. This explains why bulky particles have a sharp transition and ground particle shave a smoother one; the latter is much less volumetric constrained than the former. An outcome of such behavior is observed as strain development during the phase transition; this strain was calculated applying the Williamson-Hall method. The strain development is much more significant in the ferromagnetic phase than in the paramagnetic one, which is attributed to the weakening of the magnetic interactions as the ferromagnetic phase approach the transition. This is speculated as a decrease of the bulk modulus of the ferromagnetic phase as the temperature increases. The paramagnetic phase, however, is expect to have a relatively constant bulk modulus as there is no magnetic interactions. When observing the microscopy images, they show that cracks are usually somehow connected to a minor La-rich secondary phase observed as inclusions in the grain boundaries. It is argued that this phase is the only brittle and hard phase that does not present a volume change. Therefore the decrease of this phase, however low content it is, could lead to an improvement in the mechanical stability of the material during application. Finally the Bean-Rodbell model is applied to the describe the volumetric behavior observed through X-ray measurements as a function of the temperature. The model describes with good agreement the volume discontinuity across the phase transition, and the superimposed distribution of Curie temperature can describe well the paramagnetic growth as the transition occurs. However, the model over-predicts the thermal hysteresis and under-predicts the shift of the the transition temperature with magnetic field.

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