Magnetocalorics and magnetism in MnFe(P, Si, Ge) materials

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Chapter 3

Experimental methods

3.1 Sample preparation

In this work, all samples were prepared by ball milling from Fe$_2$P, P, and Fe powder mixed with Mn, Ge, and Si chips. In general, polycrystalline compounds were synthesized by high-energy ball milling in vacuum up to $10^{-7}$ mbar. In order to obtain homogeneous samples, the starting materials were ball milled for about one week until the steady state is obtained. During the milling process solid-state reactions are initiated through repeated deformation and fracture of the powder particles. After ball milling, the powder was pressed into pellets and sealed in quartz ampoules under 100-200 mbar argon atmosphere. Then, the ampoules were sintered at 1000-1200 °C for 5-10 hours, followed by annealing at 550-850 °C for 50 hours. Finally, they were slowly cooled down to room temperature. In the whole process, the heating and cooling rate was 180 °C per hour.

3.2 Experiment and equipments

3.2.1 Sample making

Ball-milling: Figure 3.1 shows a high energy vibratory ball milling system in high vacuum. Two samples can be milled simultaneously under the same time and vacuum milling conditions. The milled sample amount in this work varied from about 5 to 11 g. The milled samples are contained in a steel vial filled with argon gas in a glove box in order to prevent oxidization. This system works in vacuum down to $10^{-7}$ mbar. The
milling time is automatically registered and the vibration amplitude can be easily adjusted.

![High-energy vibratory ball milling system](image1)

**Figure 3.1:** *High-energy vibratory ball milling system*

A picture of the ball mill and its cross-section are shown in Fig. 3.2. A larger stainless-steel vial with a hardened-steel bottom was used. Inside this vial, there is a single hardened-steel ball with 6 cm diameter weighing 800 g. This ball is kept in motion by a water-cooled vibrating frame.

![Ball mill and cross section](image2)

**Figure 3.2:** *Ball mill (on the left) and its cross section (on the right)*
Hydraulic pressing: After ball milling for a sufficient time, the milled powder was divided into several parts for different annealing conditions, and each part was pressed into a pellet in order to have a more compact sample for heat treatment. In this work, a hydraulic pressing system at room temperature was used. The device is easily manually operated and the maximum pressure is 8 Ton.

Ampoule making: After pressing, the pellets are sealed inside quartz ampoules under 100-200 mbar argon atmosphere. This task was performed by the glass-blower department. Nowadays, fourteen ampoules can be made at the same time under the same condition of vacuum and different pressures of Ar atmosphere.

Sample annealing: There are several furnaces at the Van der Waals-Zeeman Institute (WZI) including mufflers, vertical and horizontal tubes. They reach a maximum temperature of about 1250 °C. The furnace presents a temperature gradient, the area where the samples are placed is called hot zone. In the hot zone the temperature lies within 5 degrees of the set temperature, and the length of such zone is about 10 cm for the vertical and about 15 cm for the horizontal furnaces. All furnaces are controlled by an integrated user-friendly Windows-based furnace manager program. It is in these furnaces that the samples undergo a heat treatment process in order to obtain crystalline samples.

3.2.2 Powder x-ray diffractometer
In this work, a Philips PW-1700 powder diffractometer with Cu-Kα radiation, was used to measure the diffractograms of the samples. The equipment is placed at WZI. In principle, the diffractograms of the samples were measured following the Debye-Scherrer method [1]. The measured diffractograms of the samples are compared with the calculated ones of the right material and structure. In this way one can determine if the samples have the right crystal structure, also information on the presence of second phases and state of crystallinity are obtained. The X-ray data give knowledge about the samples concerning crystal structure, crystallinity, amount of other phases and their determination, size of grains and porosity, etc.... The most widespread use of x-ray powder diffraction is for the identification of crystalline compounds by their diffraction pattern. The peaks due to impurities appear when there is more than 5 % of an impurity phase. Lattice parameters can be calculated by using the Philips X’pert Plus program, in order to have more accurate values, silicon powder was added as a
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standard, mixed together with the sample powder for x-ray measurement at room temperature.

3.2.3 Superconducting Quantum Interference Device (SQUID)
The SQUID system at WZI is a multipurpose SQUID-based magnetic measuring system, consisting of a 5 T superconducting magnet equipped with a Variable Temperature Insert (VTI) for measurements at temperatures between 1.7 K and 400 K. The SQUID facility in this system allows the measurement of very small signals, and can in principle be used for any measurement where small voltages have to be determined. The magnetization measurements of all the samples studied in this thesis were measured on this SQUID. The magnetization is gained by the magnetic flux change in the superconducting loop induced by the movement of the sample. More information can be found in [2]. The heat-capacity measurements in applied fields in the range from -9 T to 9 T were carried out on a MagLabEXA, which is described in the following section.

3.2.4 MagLab
The MagLab System is a multipurpose magnetic measuring system consisting of a 9 T superconducting magnet equipped with a VTI for measurements at temperatures between about 2 K and 360 K. The temperature range can be extended a little, but at the cost of much time and helium or risk of damage by overheating. The given temperature limits are rather safe.

Electrical resistivity measurements: The polycrystalline samples were cut into a bar shape (1 mm × 1 mm × 10 mm) for measurements of transport and magneto-transport properties. Magneto-transport measurements were accomplished in an Oxford Instruments Maglab-Exa magnetometer using a standard four-probe method in the temperature range 5-300 K and at magnetic fields up to 5 T. The electrical resistivity ρ is derived from the electrical resistance from $\rho = R \frac{A}{l}$, where $R$ is the electrical resistance, $A$ is the cross section of the sample perpendicular to the current direction and $l$ is the distance between the voltage contacts.

Specific heat measurements: There are several methods for the practical determination of the heat capacity of solids. Some of them are described in detail by
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Touloulian and Kraftmakher [3,4]. However, the measurements on bulk samples are usually performed by a semi-adiabatic heat-pulse method or by a so-called relaxation method. The semi-adiabatic heat-pulse method has been used for a long time for low temperature measurements. In this method, a magnetic sample of about 1 g is attached to a holder on which a thermometer is mounted. The holder and the sample are thermally isolated from the environment. The description of the method is found in [5,6]. In the relaxation method, the holder and the sample are thermally connected to a thermal bath by a weak heat link. The time constant for cooling through the heat link must be large compared to the characteristic time for the thermal relaxations within the sample, and between the sample and the holder. More information about this method can be found in [7-9].

However, specific-heat measurements on the samples in this thesis, were carried out on a home made specific-heat set-up with a temperature range from 4.2 to 350 K using a new method called “hybrid technique” [10]. This technique is a modification of the semi-adiabatic heat-pulse method in case the temperature drift of the sample after the heat pulse is not linear but exponential. This method is faster than the traditional relaxation method and the accuracy is of the order of 1%.

3.2.5 Electron Probe Micro-Analysis (EPMA)

The homogeneity and the stoichiometry of the samples were checked by Electron Probe Micro-Analysis (EPMA). Measurements are carried out on the JEOL 8621S microprobe at WZI- UvA. The principle of this equipment is that under influence of an electron beam, the atoms in the sample are excited. When returning to the original state, the atom emits a spectrum of photons. The energy of these photons depends on the energy difference of the electron levels of the atom and is characteristic for every element. The energy difference between K and L electron level gives a $K_{α}$, between M and L gives an $L_{α}$ reflection line. The photons are generated in a pear-shape volume, “excitation volume”. The wave length of the photons is used for element detection and the intensity for quantification of every element present in the sample. The electron beam scans over a polished sample and the detected backscatter electrons give information about the different elements in the sample. The higher the element number, the higher the stopping power for the electron beam and the higher the rate of backscatter electrons. With this information an image of the sample is
constructed. The contrast of an image is caused by the composition of the sample. In this way segregations and other different phases in the sample can be observed. The intensity of the photons from the sample is compared with a “standard” material of known composition and with the same elements in it. After correction for atomic number, absorption, fluorescence and dead time of the photon counter, the composition is calculated. This is also done for other phase present.

References