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Alexandre Pasko, Andras Bartok, Karim Zehani, Lotfi Bessais, Frederic Mazaleyrat, et al.. X-ray diffraction analysis of the magnetoelastic phase transition in the Mn-Fe-P-Si magnetocaloric alloy. AIP Advances, 2016, 6 (5), pp.056204. 10.1063/1.4943245 . hal-01690149

HAL Id: hal-01690149
https://hal.science/hal-01690149

Submitted on 22 Jan 2018

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X-ray diffraction analysis of the magnetoelastic phase transition in the Mn-Fe-P-Si magnetocaloric alloy

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Structural characterization of the $Mn_{1.3}Fe_{0.65}P_{0.5}Si_{0.5}$ powder is reported. The rare-earth-free magnetocaloric material was prepared by ball milling and solid-state synthesis. X-ray diffraction data were collected in a wide temperature range across the magnetoelastic phase transition. The lattice parameters and volume fractions of the paramagnetic and ferromagnetic phases were determined as functions of temperature using Rietveld fitting. The virgin effect (a delay of the phase transition on first cooling) and associated variation of lattice parameters are analyzed on the assumption of elastic constraints imposed on the paramagnetic phase by the defect structure. A simple Landau model with magnetoelastic coupling illustrates the observed first-order behavior.

I. INTRODUCTION

Room-temperature magnetic refrigeration is a new highly efficient and environmentally friendly technology that brings a viable alternative to the conventional gas compression technique. It uses permanent magnets and a working substance with magnetocaloric effect. However, important advances in the engine and materials design are still needed before the industrial applications of magnetic cooling will emerge.

In the present work we report on a structural study of the $Mn_{1.3}Fe_{0.65}P_{0.5}Si_{0.5}$ rare-earth-free magnetocaloric compound. This promising material exhibits a large magnetocaloric effect near room temperature due to a first-order magnetoelastic transition. Variation of chemical composition leads to changes in the temperature and hysteresis of the phase transition and can eventually alter its thermodynamic order[1,2]. To optimize the magnetocaloric properties, it is important to understand the phase transition mechanism and the role of spin-lattice coupling in Fe_2P-based materials. On the other hand, the magnetoelastic interactions seem to be responsible for a thermal history dependence of physical properties, which can undermine the cyclic stability in practical applications. We will consider structural aspects of the virgin effect observed in some magnetocaloric alloys[3–7].

II. EXPERIMENTAL

The $Mn_{1.3}Fe_{0.65}P_{0.5}Si_{0.5}$ compound was produced using a solid-state synthesis route. An off-stoichiometric nominal composition was chosen to avoid formation of secondary phases[1]. Pure Mn, Si, P and Fe_2P components were mixed and ground in a planetary ball mill under Ar atmosphere and high-energy conditions. Then, the material precursor was subjected to a recrystallization heat treatment at 1373 K for 2 hours followed by a homogenization annealing at 1123 K for 20 hours and slow cooling. Preparation details are given elsewhere[7]. The structural and magnetic properties of the obtained powder were studied in a temperature range from 100 to 300 K. X-ray diffraction (XRD) patterns were collected in Cu K_α

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radiation on a Bruker D8 Advance diffractometer equipped with an Anton Paar TTK 450 low-temperature chamber. The full-profile analysis of XRD spectra was performed using a Rietveld refinement software MAUD. Magnetic measurements were carried out on a Lake Shore 7400 Series vibrating sample magnetometer (VSM).

III. RESULTS AND DISCUSSION

The $(Mn,Fe)_{1.95}P_{0.5}Si_{0.5}$ compounds crystallize in a hexagonal structure with Pearson symbol $hP9$ and space group $P\bar{6}2m$. Fe and Mn atoms are situated in the $3g$ and $3f$ sites whereas P and Si atoms occupy the $2d$ and $1a$ sites[1,2]. The as-prepared powder was thermally cycled in the X-ray diffractometer through the phase transition temperature interval. A pseudocolor plot of the XRD intensity as a function of temperature on first cooling is shown in Fig. 1. The two hexagonal structures observed in the XRD spectra correspond to mutually transforming paramagnetic (PM) and ferromagnetic (FM) phases. Both phases coexist at intermediate temperatures and have distinct lattice parameters as suggested by well separated reflections (210), (300) and (002), which confirms the first-order character of the isostructural phase transition.

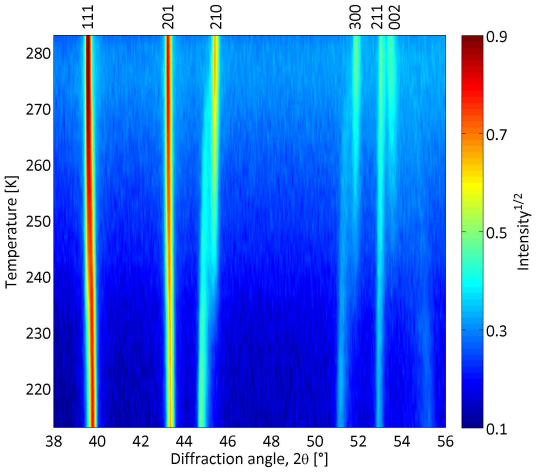


FIG. 1. A pseudocolor representation of the XRD intensity as a function of temperature on first cooling through the phase transition region of the $Mn_{1.3}Fe_{0.65}P_{0.5}Si_{0.5}$ compound.

The volume fractions and lattice parameters of the PM and FM phases have been determined using Rietveld analysis of the XRD patterns. Fig. 2 compares the temperature dependences of the FM fraction obtained from the refinement (a) and the specific magnetic moment of the sample in a constant field measured by VSM (b). The structural and magnetic data are in good agreement, including the phase transition temperature and hysteresis. It should be taken into account that the magnetic moment is proportional not only to the FM fraction, but also to the saturation magnetization vanishing at the Curie point. The striking feature of these plots is a pronounced virgin effect: the PM→FM transformation proceeds on first cooling at much lower temperatures, resulting in large hysteresis.

The lattice parameters a and c of both phases change with temperature in the opposite directions as shown in Fig. 3. In fact, the c/a axial ratio manifests an anomalous temperature dependence in a wide region around the phase transition, whereas the unit cell volume v follows a normal thermal expansion trend. The virgin effect is again present, but only the high-temperature PM phase is affected whose c/a ratio is clearly dependent on cycling history. In a first-order stable transformation cycle, the phases are in equilibrium at $T_0 = 272$ K with hysteresis $\Delta T = 2.5$ K and the following measured PM→FM jumps: $\Delta a/a = 0.5$ %, $\Delta c/c = -1.0$ %, $\Delta v/v = 0.02$ %.

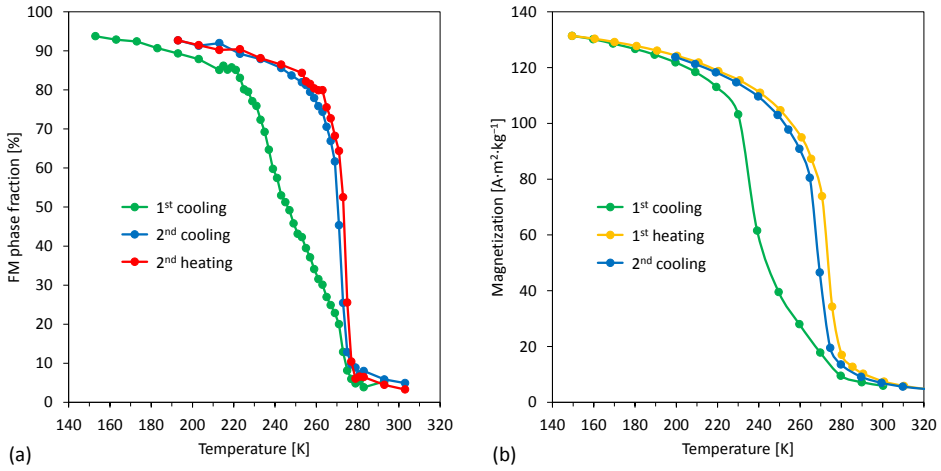


FIG. 2. Structural and magnetic characterization of the temperature-induced phase transition: (a) volume fraction of the ferromagnetic phase calculated from the XRD data; (b) specific magnetic moment in an applied field of 1 T obtained from the VSM measurements.

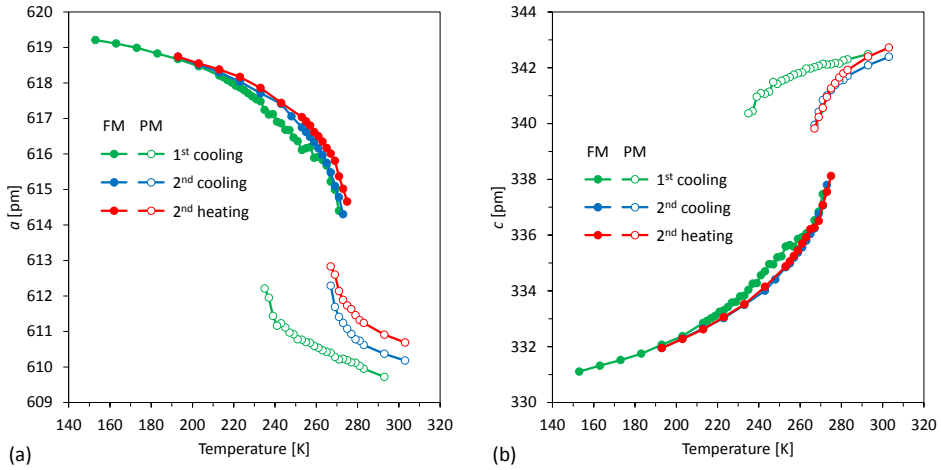


FIG. 3. Lattice parameters a (a) and c (b) of the ferromagnetic (FM) and paramagnetic (PM) phases as functions of temperature in the hexagonal $Mn_{1.3}Fe_{0.65}P_{0.5}Si_{0.5}$ compound.

To illustrate the behavior of lattice parameters during the PM↔FM phase transition in the hexagonal Mn-Fe-P-Si alloys, let us consider a simple Landau model with a coupling between the magnetic and elastic degrees of freedom. The average magnetization m will serve as the primary order parameter, whereas the shear strain (deviation of axial ratio $\eta = c/a$ from its high-temperature value, $e = \eta - \eta_0$) can be taken as the secondary macroscopic variable. The free energy of thermodynamic system reads as follows[8]:

$$F = \alpha m^2 + \beta e^2 + \gamma m^4 + \delta e^4 + \lambda m^2 e - hm, \tag{1}$$

where coefficient α is a function of temperature, constant β is assumed to be positive, factor h is magnetic field. Constants γ, δ and λ can be reduced to 1 by appropriate scaling transformation of variables m, e and F. The problem of finding the global minimum of thermodynamic potential (1) is solved numerically and presented in Fig. 4 for $h = 0$ (a) and $h > 0$ (b). Functions $m(\alpha)$ and $e(\alpha)$ are continuous when $\beta \leq 1/4$ (second order transition) and have a break point at $\alpha > 0$ when $\beta > 1/4$ (first order transition). Application of field

h results in nonzero values of variables m and e in the symmetric phase; similar feature appears when considering the effect of random fields or order parameter fluctuations.

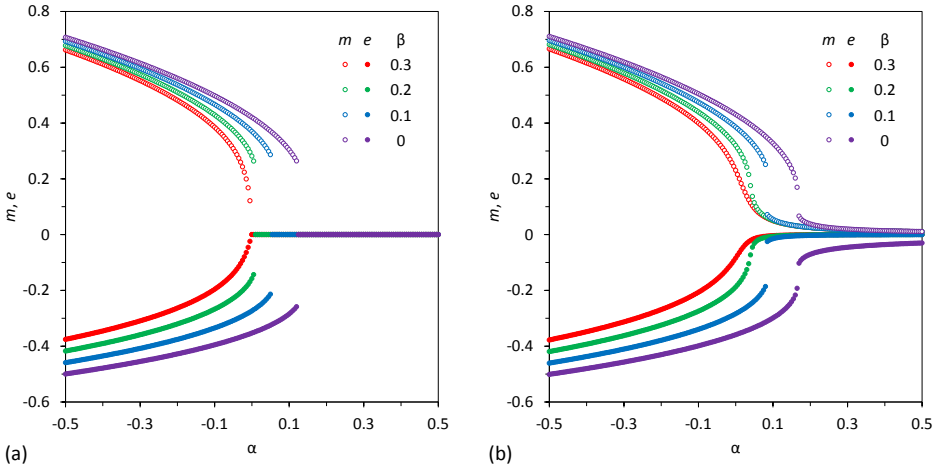


FIG. 4. Dependence of magnetization (order parameter) $m \geq 0$ and strain (coupled variable) $e \leq 0$ on temperature-dependent coefficient α in a dimensionless Landau model of magnetoelastic phase transition with applied field: (a) $h = 0$; (b) $h = 0.01$.

If we hinder strain e from changing, the PM→FM phase transition will shift to lower temperatures. This may explain the unusual behavior of lattice parameters in the virgin state. During first cooling the PM phase is constrained by grain boundaries and defect structure, the FM phase growth is accompanied by elastic fields and irreversible movement of dislocations. On further cycling the phase boundaries move along the path already made, with small hysteresis and almost no energy dissipation.

In conclusion, we presented an investigation of the phase transition in a Mn-Fe-P-Si alloy where phase coexistence is studied using structural and magnetic measurements. Comparison between the two methods is relevant because the extrapolation of phase fractions from magnetization data can be affected *e.g.* by a temperature dependence of the spontaneous magnetization. A phenomenological model is used to discuss the influence of elastic interactions of extrinsic origin on the behavior of the first ferromagnetic ordering transition, confirming some insight into the virgin effect presented in our recent paper[7].

ACKNOWLEDGMENTS

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7) under grant agreement 310748 (DRREAM).

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