Nanoscale structural rearrangement in the doped polar semiconductor $Ge_{1-x}Mn_xTe$

GeTe is an intriguing semiconductor exhibiting a huge variety of properties. The system solidifies around 730°C in a cubic structure. Upon cooling through approximately 430°C the unit cell distorts and a rhombohedral polar structure is realized, making GeTe one of the simplest ferroelectric compounds. A sketch of both unit cells superimposed in the pseudocubic setting of GeTe is shown in Fig. 1.

In spite of its classification as a semiconductor, it has a metallic resistivity with charge-carrier concentrations of the order of 10^{21} cm^{-3} thanks to unintentionally self-doped holes due to Ge vacancies. GeTe features a multivalley band structure which is responsible for the emergence of superconductivity and its role in thermoelectric devices. GeTe-related materials are also known for their phase-change memory functionality as it is utilized, e.g., in digital versatile disks (DVD). In the latter, light- / heat-pulses are used to switch the structure of the device locally between amorphous and crystalline back and forth. Here we report a magnetic analogue of this effect: Upon Mn doping GeTe becomes ferromagnetic [1] and we successfully demonstrated that as long as the system remains rhombohedral, there are two different magnetic phases as shown in the phase diagram in Fig. 2 [2]. Therein the ferromagnetic transition temperature T_c is plotted against the Mn concentration x (see Ref. 2 for details). Which magnetic phase is realized depends on the heat treatment: Slow controlled cooling ("cc") from the melt establishes a ferromagnetic phase with high ferromagnetic transition temperatures T_c up to ~180 K, while quenching ("q") from 620°C, i.e., from the cubic phase, yields T_c values which are a factor of five to six smaller around the maximum of the dome-like high-T_c phase line in Fig. 2. Upon further increasing the Mn concentration, the polar distortion of the unit cell is more and more suppressed. The heat-treatment effect disappears when the Mn doping concentration becomes sufficiently large to realize cubic crystalline symmetry even at low temperatures. As it will be discussed below, this is not a sharp structural phase transition but rather a crossover. This structural transition range is indicated in gray in Fig. 2.

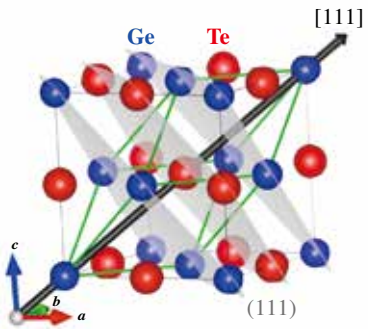

Fig. 1. Sketch of the structure of $Ge_{1-x}Mn_xTe$: The high-temperature cubic (rock-salt type) and the low-temperature rhombohedrally-distorted structures of GeTe are superimposed in its pseudo-cubic setting. The Ge and Te atoms are shown in blue and red, respectively. The gray layers are the crystallographic (111) planes and the black arrow indicates the direction of polar distortion, i.e., the cubic [111] direction.

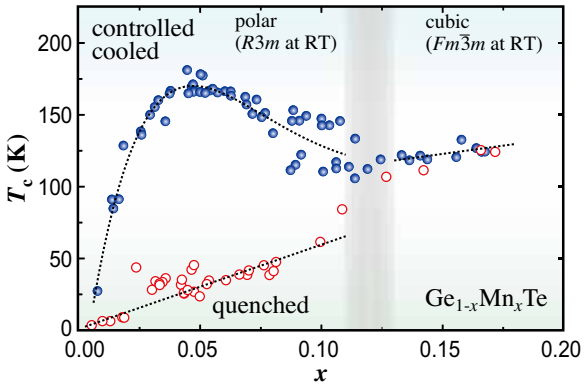

Fig. 2. Magnetic phase diagram of $Ge_{1-x}Mn_xTe$: The ferromagnetic transition temperature T_c is plotted vs the Mn concentration x. The filled blue symbols give the ferromagnetic T_c of controlled-cooled, the open red symbols of quenched samples. The gray shaded area indicates the structural crossover x range where the structure changes doping-induced from rhombohedral to cubic even at low temperatures. Dotted lines are guides to the eyes.

Apparently the rhombohedral distortion is essential for the observation of these two distinct ferromagnetic phases. To gain insight how the two different heat-treatment recipes affect the structure of $Ge_{1-x}Mn_xTe$, we measured various samples throughout the phase diagram at SPring-8 **BL44B2**. An analysis of the high-resolution synchrotron XRD patterns in combination with EDX measurements revealed (see Ref. 2), that quenched low-T_c samples exhibit a comparably homogeneous Mn distribution throughout a sample while controlled-cooled high-T_c samples are characterized by strong Mn inhomogeneity and the formation of Mn-rich regions. Exemplarily, XRD data on a magnified view of the cubic 220_c reflection around $2\theta \approx 13.5°$ are shown for four selected samples in Figs. 3(a) and 3(b): (a) x = 0.050, T_c = 24 K, "q" (red data) and x = 0.047, T_c = 171 K, "cc" (blue data); (b) x = 0.166, T_c = 125 K, "q" (red) and x = 0.164, T_c = 127 K, "cc" (blue). The big difference between quenched and controlled-cooled rhombohedral samples is that quenched samples exhibit rather sharp

reflections as seen in Fig. 3(a). The two peaks in the red data are identified as the 104_h and 110_h reflections (in hexagonal setting) as expected for rhombohedral GeTe. In contrast, the 104_h reflection of the similarly doped controlled-cooled sample shown in blue in Fig. 3(a) has split into two peaks of lower intensity. There is also a shoulder visible around $2\theta \approx 13.5°$ and the 110_h peak has broadened as compared to the data of the quenched sample. The 104_h reflection contains information about the degree of the rhombohedral distortion, i.e., a broadening or even splitting of this reflection indicates that the degree of the rhombohedral distortion changes throughout the sample. We interpret this as an indication of the formation of different domains in controlled-cooled samples which obey the same global rhombohedral symmetry but exhibit varying distortion angles. For simplicity we assume here only two differently distorted domains labeled "*R*1" and "*R*2" in Fig. 3(a). The domain *R*1 is assumed to be strongly distorted and hence the corresponding XRD reflection is seen at a lower angle. This domain does not contain much Mn dopants and is similar to pristine GeTe. On the other hand, *R*2 is only weakly distorted and consists of the aforementioned Mn-rich regions.

As for the data of the quenched and controlled-cooled samples with larger Mn concentrations shown in Fig. 3(b), there is only one sharp peak visible for each of them (again red data was taken on a quenched, blue data on a controlled-cooled sample). Both samples are cubic and the respective 220_c reflections are comparable, i.e., there is no clear difference in the XRD patterns any more between controlled-cooled and quenched samples.

The underlying mechanism here is a spinodal decomposition. When cooling a sample which is rhombohedral at room temperature in a controlled and slow manner from its cubic high-temperature phase, the Mn ions agglomerate and form the weakly distorted phase fractions *R*2. The latter are several 10 nm in diameter and as discussed in more detail in Ref. 2, *R*2 is responsible for the emergence of the high-T_c phase. The clustering leads to a very inhomogeneous situation with Mn-rich regions embedded in a Mn-poor almost pristine GeTe matrix. Upon further Mn doping, the Mn concentration becomes locally so large that some *R*2 domains switch into cubic structure. This probably starts to happen around the maximum of the dome-like high-T_c phase line in Fig. 2, i.e., as soon as cubic phase fractions in controlled-cooled samples appear, the ferromagnetic T_c is suppressed. On the other hand, in quenched samples there is no time to allow for a relocation of Mn ions and hence a much more homogeneous situation is established. In this sense the homogeneous Mn distribution in the cubic high-temperature phase is "frozen" although the crystal nevertheless distorts rhombohedrally upon quenching. We identify this more homogeneous situation with a large single matrix of *R*1 phase fraction. The ferromagnetism in this low-T_c phase is understood in a Rudermann-Kittel-Kasuya-Yoshida (RKKY) framework. When a sample is sufficiently doped so that the structural transition to cubic has completed, there is no difference in the ferromagnetism any more between samples grown by either cooling recipe, i.e., both heat treatments yield a homogeneous arrangement of the Mn dopants.

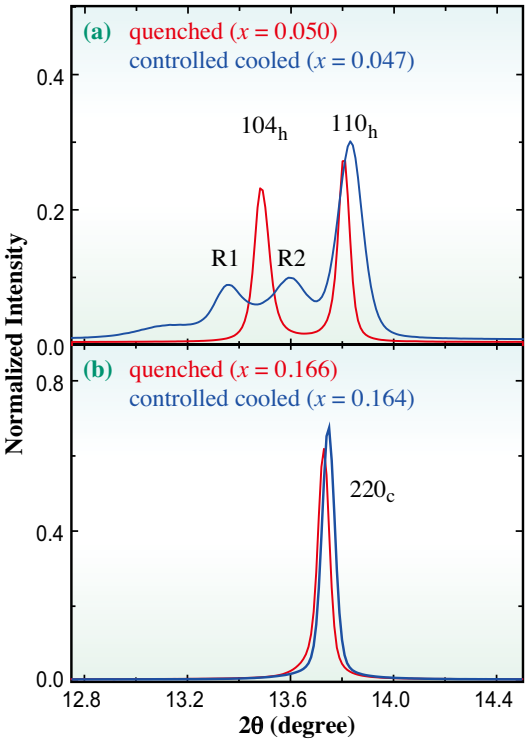

Fig. 3. XRD data taken at SPring-8 of **(a)** a quenched (red, $x = 0.050$) and a controlled-cooled rhombohedral sample (blue, $x = 0.047$) around the (104) and (110) reflections (hexagonal setting) and **(b)** a quenched (red, $x = 0.166$) and controlled-cooled cubic sample (blue, $x = 0.164$) around the corresponding single cubic (220) peak. The labels *R*1 and *R*2 mark an additional peak splitting due to differently distorted rhombohedral phase fractions, see text.

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