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## Order-disorder transformations in Sm–Co and Sm–Co–ZrC systems with 2-17 stoichiometry

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This work investigates the order-disorder transformations utilizing time-resolved x-ray diffraction at the Advanced Photon Source. The metastable phases that can form during the order-disorder transformations in the Sm–Co intermetallics have the potential to produce materials with enhanced permanent magnetic properties. The high-temperature experiments transformed the disordered alloys with the TbCu<sub>7</sub>-type structure obtained by rapid solidification into the mixture of the hexagonal and rhombohedral ordered structures at 1375 K. The ordering process and the role of the ZrC alloying on the phase formation and ordering transformations were examined. The results showed the formation of shoulders of the fundamental peaks and superlattice peak broadening prior to complete ordering. The lattice parameters expanded linearly up to the onset of ordering, after which an abrupt change of slope was observed. The change in slope suggests a nucleation and growth mechanism for the ordering transformation. The effect of ZrC alloying promoted the formation of the disordered structure in the as-solidified state and lowered the onset of the ordering temperature. © 2007 American Institute of Physics. [DOI: 10.1063/1.2712525]

### INTRODUCTION

The transformation from the metastable to equilibrium phases is critical for the development of the proper microstructures in order to optimize the properties in the Sm–Co-based magnets.<sup>1–6</sup> The pertinent transformation involves going from a disordered to an ordered state. Therefore, understanding the formation of order in these systems from the disordered precursors is of the great significance. Furthermore, the development of atomic arrangements can have an impact on intrinsic magnetic properties such as magnetization and Curie temperature. The order/disorder is attributed to the degree of the periodic arrangement of the metallic pairs of atoms—dumbbells. The ordered state with the precise dumbbell location offers two polymorphs: rhombohedral with Th<sub>2</sub>Zn<sub>17</sub>-type structure (2-17R) and hexagonal with Th<sub>2</sub>Ni<sub>17</sub>-type structure (2-17H).<sup>4</sup> In the disordered state, the metastable TbCu<sub>7</sub>-type structure (1-7) forms in which dumbbells are randomly distributed throughout the lattice.<sup>2</sup> Previous studies have identified the existence of the intermediate metastable phase in the Sm<sub>2</sub>Co<sub>17</sub>–NbC system, where the appearance of a shoulder on the (101) fundamental peak in the disordered 1-7 phase and the (21-2) superlattice peak at 1023 K prior to complete ordering suggested the formation of the longer-range order with a period of 3.6 nm (or three times the *c* axis).<sup>3</sup> However, the quench-and-anneal technique utilized does not allow for the observation of subtle structural transformations; moreover, the precipitation of other phases upon quenching can also overshadow the presence of the intermediate structures. In other systems the formation of the equilibrium 2-17 structure was suppressed by the addition of the alloying elements, for example, in the

Sm<sub>2</sub>Fe<sub>17</sub>–TiC system, the alloying addition significantly reduced the onset of ordering compared to the binary Sm–Fe.<sup>6</sup> It was suggested that Ti occupies Fe dumbbell sites by creating the Ti/vacancy pairs, which inhibit ordering. In order to investigate the structural transformations in Sm–Co and related alloys, high-temperature time-resolved powder diffraction experiments were conducted at the Advanced Photon Source synchrotron facility.

### EXPERIMENTAL PROCEDURE

The rapidly solidified Sm<sub>11</sub>Co<sub>89</sub> and (Sm<sub>0.11</sub>Co<sub>0.89</sub>)<sub>94</sub>Zr<sub>3</sub>C<sub>3</sub> were obtained by first arc melting the high purity (>99.9) elements and subsequent melt spinning of the 10 g ingots in an argon atmosphere with the tangential wheel velocity of 40 m/s. The melt-spun ribbons were crushed into powder and sealed under argon in small capillaries. The time-resolved high-temperature x-ray diffraction experiments were carried out at the beamline 6-ID at the Advanced Photon Source, Argonne National Laboratory utilizing synchrotron radiation with incident energy of ~80 keV ( $\lambda \approx 0.1234$  Å). The experimental setup utilized the Debye-Scherrer geometry. The capillaries were placed in a specially designed furnace,<sup>7</sup> and the x-ray images were collected every 10 s with the MAR charge coupled device (CCD) camera at a heating rate of 10 K/min. Further, the data were reduced to the full x-ray diffraction scans with *q* ranging from 10 to 70 nm<sup>-1</sup> using the FIT2D software.<sup>8</sup> The Rietveld refinements were conducted for phase data analysis using the GSAS software package.<sup>9,10</sup> The lattice parameters, atomic coordinates, occupancies, thermal parameters, peak profiles, and phase fractions were refined simultaneously.

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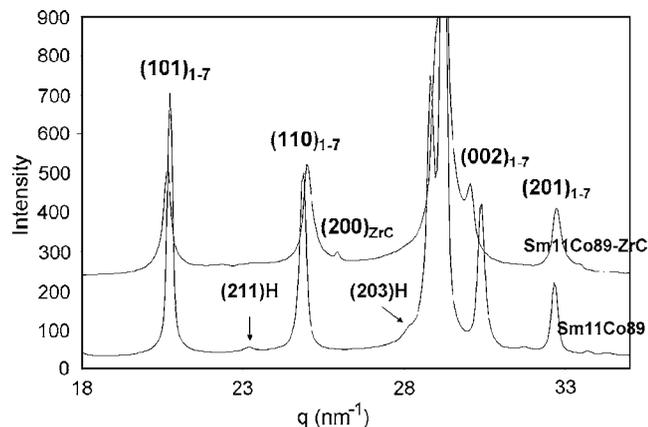


FIG. 1. X-ray diffraction scans of the rapidly solidified  $\text{Sm}_{11}\text{Co}_{89}$  and  $\text{Sm}_{11}\text{Co}_{89}\text{-ZrC}$  alloys exhibiting the disordered  $\text{TbCu}_7$ -type structure.

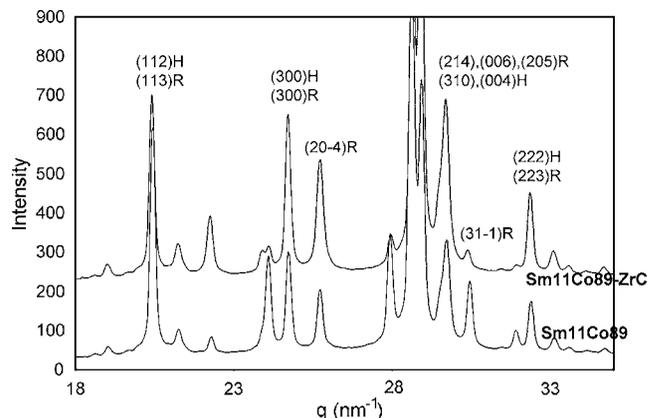


FIG. 2. X-ray diffraction scans of  $\text{Sm}_{11}\text{Co}_{89}$  and  $\text{Sm}_{11}\text{Co}_{89}\text{-ZrC}$  alloys at 1375 K exhibiting the combination of the ordered 2-17R and 2-17H phases.

## RESULTS AND DISCUSSION

The x-ray diffraction results indicated that the as-solidified  $\text{Sm}_{11}\text{Co}_{89}$  and  $\text{Sm}_{11}\text{Co}_{89}\text{-ZrC}$  alloys corresponding to the 2-17 stoichiometry primarily formed with the disordered 1-7 structure for both alloys (Fig. 1). The  $\text{Sm}_{11}\text{Co}_{89}$  also contained a small amount of the 2-17H phase as indicated by the presence of the (211) and (203) superlattice peaks. The 2-17H has a more simple ordered structure than the 2-17R, and it is usually stable at high temperatures; as a result, its presence here may be because the cooling rates are not sufficient to suppress formation of all long-range ordering. The 2-17H was not observed in the ZrC containing alloy, suggesting that the addition of ZrC suppresses the long-range ordering. Analysis of the lattice parameters revealed that the addition of ZrC resulted in an expansion of the  $c$  axis and contraction of  $a$  axis of the unit cell, indicating that at least some of the Zr and C went into solution.

The x-ray diffraction patterns showed that the transformation to the ordered structures occurred at elevated temperatures (Fig. 2). At 1375 K, both alloys contained a mixture of the 2-17R and 2-17H phases. However, the reported Sm-Co phase diagram<sup>11</sup> indicated that the hexagonal phase is only stable above 1553 K. Here, the 2-17H appears 178 K lower, and is present in the mixture with the 2-17R, indicating the coexistence of the two phases.

Monitoring of the lattice parameters can provide insight into when the transformation begins as well as other features of the transformation. The lattice parameters of the 1-7 unit cell are related to those of the 2-17R as follows:

$a_{2-17} = \sqrt{3}a_{1-7}$  and  $c_{2-17} = 3c_{1-7}$ .<sup>2</sup> For ease of discussion, the lattice parameters are reported here based on the 2-17R unit cell. Figure 3 presents the change of the  $a$  and  $c$  lattice parameters as a function of temperature obtained during the sequential GSAS refinements. The initial linear increase in the lattice parameters observed in both samples was caused by the linear expansion of the unit cell; however, at elevated temperatures the dramatic departure from linearity has been observed, suggesting that structural changes accompany the ordering process. This suggests that the transformation to the ordered structure occurs via nucleation and growth. In  $\text{Sm}_{11}\text{Co}_{89}$  the deviation from linearity occurs in the range of 1087 ( $a$ -lattice parameter)–1091 K ( $c$  parameter). Another inflection point was also observed at 1176 K for both  $a$ - and  $c$ -lattice parameters. The exact origin of the deviation at 1176 K is not understood, although it could be related to the onset of the formation of the 2-17H variant. Further work is necessary to more clearly understand the origin of this inflection. In the  $\text{Sm}_{11}\text{Co}_{89}\text{-ZrC}$  system, the initial deviation from linearity occurs in the range of 1065–1076 K (for  $a$  and  $c$ , respectively). It was also not possible to achieve the satisfactory curve fitting during the GSAS sequential refinements over the temperature range where the ordering transformation was taking place. A closer look at the x-ray diffraction patterns provides more details into the structural changes that coincide with the changes in the lattice parameters (Figs. 4 and 5).

In  $\text{Sm}_{11}\text{Co}_{89}$ , the initial onset of ordering is indicated by the formation of a shoulder on the low-angle side of the

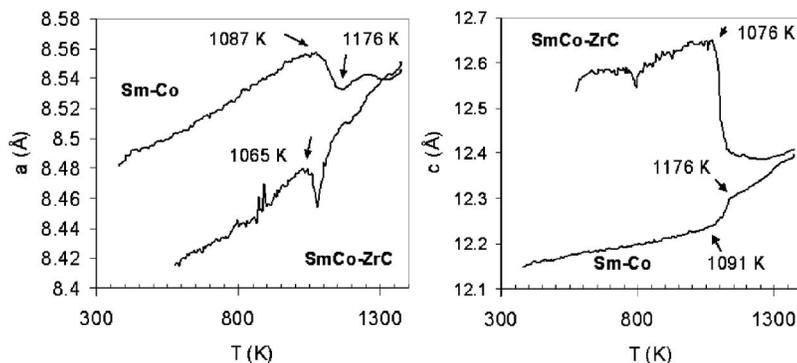


FIG. 3. The behavior of the  $a$ - and  $c$ -lattice parameters of the 2-17R ordered phase during heating of the  $\text{Sm}_{11}\text{Co}_{89}$  and  $\text{Sm}_{11}\text{Co}_{89}\text{-ZrC}$  alloys.

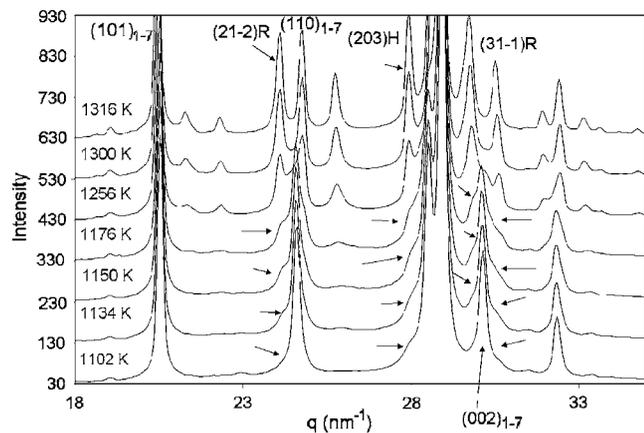


FIG. 4. X-ray diffraction scans of the  $\text{Sm}_{11}\text{Co}_{89}$  alloy in the 1102–1316 K temperature range demonstrating the occurrence of the ordering transformation via formation of shoulders (arrowed) at the superlattice peak positions.

(110) 1-7 peak. The superlattice (21-2) peak develops from this shoulder. The (002) 1-7 fundamental peak also exhibits unusual features. First, shoulders were observed on both sides, easily evident at 1134 K. The high-angle shoulder eventually developed into the (31-1)R peak. Finally, the fundamental (002) peak shifted to the lower angle, reflecting the expansion of the  $c$  axis observed in Fig. 3. The initial shoulders reflect the breadth of the superlattice peaks in the early stages of ordering. The width of the superlattice peak is dependent on the size of the ordered regions also known as antiphase domains.<sup>12</sup> As the domains grow, the peaks sharpen, leading to distinct superlattice reflections. The 2-17H phase was present in the as-solidified sample, but its further development also occurs at elevated temperatures, as shown by the formation of the low-angle shoulder of the (203)H peak.

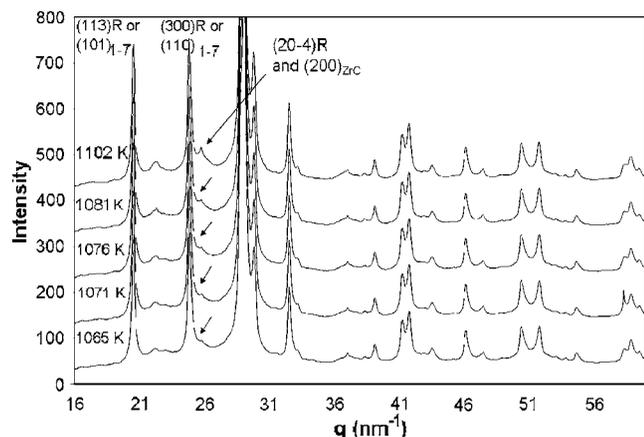


FIG. 5. X-ray diffraction scans of the  $\text{Sm}_{11}\text{Co}_{89}\text{-ZrC}$  alloy in the 1065–1102 K temperature range demonstrating the initial stages of shoulder development (arrowed) at the onset of the ordering transformation.

In the ZrC-alloyed sample, the ordering transformation starts at 1065 K, which is 25 K lower than in the binary system. The onset is evidenced by displaying a high angle shoulder of the (110) 1-7 fundamental peak. This is the only shoulder observed. The formation of the 2-17H did not start until 1170 K. This is still well below where the phase diagram shows the 2-17H phase onset to be.

## CONCLUSIONS

The time-resolved high-temperature experiments utilizing the synchrotron radiation was used to explore the order-disorder transformations occurring in Sm-Co and Sm-Co-ZrC systems with the 2-17 stoichiometry. The disordered as-solidified alloys with the  $\text{TbCu}_7$ -type structure were transformed into the mixture of the 2-17H and 2-17R at elevated temperatures. The formations of shoulders of the fundamental peaks and departure from linearity of the lattice parameters in these systems have been observed. The effect of ZrC alloying promoted the formation of disordered structure, but reduced the temperature at which ordering began. The evolution of the lattice parameters during the transformations exhibited the nonlinearity, suggesting the nucleation and growth mechanism during ordering.

## ACKNOWLEDGMENTS

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