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Orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase revisited

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Letter

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ABSTRACT

The structure of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase was revisited in the present work. Selected-area electron diffraction (SAED) and high-resolution electron microscopy (HREM) techniques were used to investigate the structure. They show the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase has a 1-D incommensurate modulated structure. The structure can be approximately described as a B-centered orthorhombic lattice. The lattice parameters of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase have been determined by a tilt series of SAED patterns. A hexagonal network with a modulation wave has been observed in the HREM image and the hexagonal motif is considered as the basic structural unit.

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1. Introduction

The $\text{Zr}_2\text{Co}_{11}$ intermetallic compound and its magnetic properties have been studied since 1990 [1–11]. Since rare-earth-free permanent-magnets have gained immense focus from the viewpoint of mitigating the critical-material aspects of rare-earth elements, the $\text{Zr}_2\text{Co}_{11}$ intermetallic compound is considered as one of the promising candidates due to the strong magnetocrystalline anisotropy energy of 1.1 J cm^{-3} and high Curie temperature of about 500°C [3,4]. Intensive studies were aimed at understanding and improving the magnetic properties of $\text{Zr}_2\text{Co}_{11}$ and related compounds [5,6 and references cited therein] but only a few studies focused on the crystal structures of the $\text{Zr}_2\text{Co}_{11}$ compound [7–11].

The crystal structure of the $\text{Zr}_2\text{Co}_{11}$ intermetallic compound was studied by Demczyk and Cheng [7] using the combination of SAED and convergent-beam electron diffraction (CBED) methods. An orthorhombic unit cell was determined, which was interpreted as an antiphase structure of two long-period superlattices in relation to one another along [001]. A different set of lattice parameters of the orthorhombic phase was given by Gabay et al. [8] based on their SAED work. An X-ray diffraction analysis of a sample with a large grain as a single crystal by Ivanova et al.

[9] revealed that the compound has a rhombohedral structure at high temperatures and an orthorhombic structure at a relatively low temperature. Evidence for a hexagonal, high-temperature phase also was observed [9]. Incommensurate modulation in the structure of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase was noticed in the study of the microstructure [10]. The lattice parameters of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase in the literature are listed in Table 1.

Recently a systematic adaptive genetic algorithm (AGA) crystal-structure search has been developed and applied to the $\text{Zr}_2\text{Co}_{11}$ compound [11]. It has been found that all the lowest-energy structures, except ZrCo_5 , share a common structural motif, which can be viewed as a derivative of the SmCo_5 structure with some modifications. The structures of the three $\text{Zr}_2\text{Co}_{11}$ phases reported by Ivanova et al. [9] were reconstructed by using the primitive cell from the AGA search. The predicted structures were checked with the experimental X-ray powder diffraction (XRD) diagrams and the model of the rhombohedral phase was also compared with experimental SAED patterns and HREM images.

In our recent work on the improvement of the magnetic properties of the Zr–Co and related systems [5,6], the structure of the $\text{Zr}_2\text{Co}_{11}$ compound was revised. In this paper, the crystal lattice of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase has been determined by a tilt series of SAED patterns and the basic structural motif and modulation wave have been revealed in the HREM images.

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Table 1

The lattice parameters of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase. The b and c parameters in Refs. [8–10] are exchanged here for easy comparison.

No.	a (nm)	b (nm)	c (nm)	Reference
1	0.48	0.82	3.6	[7]
2	0.47	2.42	3.3	[8]
3	0.471	2.42	1.67	[9,10]
4	0.47	0.82	(3.6)	Present work ^a

^a The incommensurate modulation exists in the c axis of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase, so the $c \approx 3.6$ nm is given here for the periodic approximant in the present work.

2. Experimental

Ingots of $\text{Zr}_x\text{Co}_{100-x}$ ($x = 16, 17, 18, 19$ and 21) were arc melted from high-purity elements in an Ar atmosphere. The ribbons were made by ejecting molten alloys in a quartz tube onto the surface of a copper wheel with speeds from 5 to 60 ms^{-1} . The process parameters such as ejection pressure, diameter of the quartz tube hole, melting time and distance between quartz tube and the surface of copper wheel were optimized for obtaining high-quality ribbons [5,6]. The ribbons are about 2 mm wide and 50 μm thick.

Selected ribbons were cut into pieces approximately 2 mm long and mechanically ground and polished to approximately 30 μm or thinner. Following mounting onto 3 mm diameter Cu or Mo rings, samples were further ion-beam (Ar^+) milled to electron transparency. Transmission electron microscopy (TEM) experiments were carried out on JEOL JEM2010 and FEI Tecnai Osiris microscopes. Both of them are operating at 200 kV and equipped with a double-tilt stage and energy-dispersive X-ray spectroscopy (EDS) detectors. Crystalline phases were first identified with SAED and EDS experiments, followed by a tilt series of SAED patterns and HREM images on selected crystalline grains. Simulated SAED patterns were calculated using Project/SAED2 [12] and experimental SAED patterns were measured using JEC/PSAED [13] and JEC/UnitCell2 [14] software.

3. Results and discussion

The lattice parameters of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase in the literature were determined mostly using SAED patterns. The discrepancy of the lattice parameters is probably due to the existence of two polymorphic phases with closely related structures. As pointed out in Ref. [9], some SAED patterns of the rhombohedral $\text{Zr}_2\text{Co}_{11}$ phase may be mistakenly interpreted as belonging to the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase and vice versa. Thus the lattice parameters are hard to determine convincingly from the SAED patterns from various grains even in the same sample. One way to overcome the problem is to use a tilt series of SAED patterns from the same grain to uniquely reconstruct the reciprocal lattice.

Fig. 1(a–c) shows a tilt series of SAED patterns from the same grain of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase; all patterns keep the same c^* axis and the tilting angles of the patterns of A, B and C are 0° , 16° and 30° . Fig. 1(d) shows the reconstruction of the reciprocal lattice with the c^* perpendicular to the view plane, and the directions of a^* and b^* of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase are marked. Extra diffraction spots from twinned grains are noticeable in Fig. 1(a–c). These spots were neglected during the determination of the lattice type and parameters. The lattice parameters of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase are calculated by the JEC/PSAED software and listed in Table 1. The calculated angles between A–B and A–C are 15.6° and 30.0° . Two noticeable features are that the incommensurate modification exists along the c^* axis and that the $[110]$ pattern looks similar to the $[010]$ pattern.

The $[010]$ SAED pattern of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase is enlarged in Fig. 2(a), in which strong diffraction spots are marked with arrows to indicate a pseudo-hexagonal symmetry. In order to elaborate the feature of the modulation along the c^* axis, the distribution of the diffraction spots was analyzed using JEC/PSAED; an intensity profile mapping to the intensity distribution between two strong spots (pointed with arrows), from 1 to 2 and from 2 to 1 were obtained in Fig. 2(b and c). The same periodic spacing lines

Fig. 1. (a–c) A tilt series of SAED patterns of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase and (d) the reconstruction of the reciprocal lattice with the c^* perpendicular to the view plane.

Fig. 2. (a) An enlarged $[010]$ SAED pattern of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase. The intensity profiles are obtained (b) from spot 1 to spot 2 and (c) from spot 2 to spot 1. The periodic distribution of the diffraction spots exists locally but lost in the whole pattern.

Fig. 3. (a) HREM image of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase taken with the incident electron beam along [010] zone axis. (b) A schematic drawing of a perfect hexagon as a basic structure motif, which can be described as (c) a base-centered rectangular unit cell. (d) Schematic drawing of the periodic approximant of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase as revealed in (a).

are applied to the two figures to reveal the periodicity. The peaks on the left side match to the period but the peaks on the right side slightly mismatch to the periodicity. This means that the periodicity exists locally only. In other words, the periodicity exists among the local spots around the basic strong spots but is lost in the whole pattern.

The diffraction pattern of a modulated structure can be indexed using more than three indices as follows [15]:

$$\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}^* \quad (1)$$

$$\mathbf{q}^* = q_1\mathbf{a}^* + q_2\mathbf{b}^* + q_3\mathbf{c}^* \quad (2)$$

For the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase, $q_1 = 0$, $q_2 = 0$, $q_3 = 0.074$. The main lattice is a pseudo hexagonal lattice, which can be described as a base-centered orthorhombic lattice with $a = 0.47$ nm, $b = 0.82$ nm and $c = 0.27$ nm.

A HREM study was carried out to further study the structure of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase. Fig. 3(a) shows a HREM image taken with the incident electron beam along [010] zone axis, which can be described as a network of dots grouped in perfect and deformed hexagons. A schematic drawing of a perfect hexagon is given in Fig. 3(b). The hexagon can thus be viewed as a basic structural motif and the modulation wave is formed by a periodic alternation of the perfect and deformed hexagons. In considering the symmetry of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase, the hexagonal motif should be described as a base-centered rectangular unit cell in Fig. 3(c). A rectangular box with dimension of 0.47 nm and 3.6 nm in Fig. 3(a) was marked to describe the incommensurate modulated $\text{Zr}_2\text{Co}_{11}$ phase approximately as a periodic lattice. The near perfect hexagons at the corners and center are outlined in Fig. 3(a and d). This means that the periodic approximant is a B-centered lattice with $a = 0.47$ nm, $b = 0.82$ nm and $c = 3.6$ nm, which also explains with the extinction rules in the SAED patterns pointed out in Ref. [7].

The lattice parameters of the periodic approximant are in agreement with the results in Ref. [7]. For convenience in comparison, the b and c axes in Refs. [9,10] are exchanged here [see note in Table 1], $a = 0.471$ nm, $b = 2.42$ nm and $c = 1.67$ nm. The lattice parameter a is in agreement each other in all the work. The lattice parameter b in Refs. [9,10] is about triple of the value in present work and the $c \approx 2\sqrt{3}a$ in Refs. [9,10] while $c \approx 13a/\sqrt{3}$ in the present work.

Twin structure has been observed in the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase [9]; however, the twin structure was shown in SAED patterns of relatively higher zone axes and the details of the twin boundary were not given. Fig. 4 shows (a) an SAED pattern of twinned orthorhombic $\text{Zr}_2\text{Co}_{11}$ structures along the [010] zone axis and (b) the simulation based upon a one-atom-motif B-centered periodic approximant. The calculated electron diffraction pattern shows some features of the positions of the strong

Fig. 4. (a) An SAED pattern of twinned orthorhombic $\text{Zr}_2\text{Co}_{11}$ structures along the [010] zone axis, (b) the simulated pattern based upon a one-atom-motif B-centered orthorhombic approximant.

Fig. 5. HREM image of a twin boundary of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase taken with the incident electron beam along the [010] zone axis. A coherent twin boundary shares the common structural motifs.

diffraction spots in the experimental pattern. The positions of the weak diffraction spots and the diffraction intensities cannot be reproduced due to the over simplified model. The HREM image in Fig. 5 shows the twinned grains of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase. A coherent twin boundary is marked by a zigzag line. The formation of twinned interface can be interpreted as the twinned grains sharing the common hexagonal structural motifs.

The lattice parameters of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phases are closely related to those of the rhombohedral $\text{Zr}_2\text{Co}_{11}$ phase and the formation of the twin structure of the former resembles the unique axis of the latter. As pointed out in Ref. [9], these facts may provide a hint of the phase transformation from the rhombohedral $\text{Zr}_2\text{Co}_{11}$ phase to the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase. On the other hand, it should be pointed out that no coexistence of the two phases side-by-side was observed in the present work.

Structural models of the orthorhombic and rhombohedral $\text{Zr}_2\text{Co}_{11}$ phases have been constructed using a common structural motif, which was derived from a systematic adaptive genetic algorithm search using first-principles calculations [11]. The simulations based on the model of the rhombohedral $\text{Zr}_2\text{Co}_{11}$ phase were in a good agreement with the experimental results of XRD diagram, SAED patterns and HREM images. This indicates that the structural model is very successful. The structural model of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase was constructed based on the lattice parameters in Refs. [9,10] and the simulated XRD diagram based on the model was found in agreement with the experimental XRD data. It is not surprising that a structural model could be constructed by the same motif and the present lattice parameters, and the simulated XRD diagram will give a similar result due to the relation of the two sets of the lattice parameters. However, the hexagonal motifs, revealed as near perfect and deformed hexagons

in the HREM image, cannot be found in the projection of the predicated orthorhombic structure in Ref. [11]. Thus the structural motif in Ref. [11] cannot be directly used to interpret the HREM image in Fig. 3(a). This means that the structure of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase might be closely related to the structure of the rhombohedral $\text{Zr}_2\text{Co}_{11}$ phase, but they are not built from exactly the same structural motif.

4. Conclusions

In the present work, SAED and HREM techniques were used to study the structure of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase. The lattice type and parameters of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase have been determined. A hexagonal basic structural unit and 1-D incommensurate modulation wave have been identified. The twin relation and twin boundary have been investigated. Structure feature of the orthorhombic $\text{Zr}_2\text{Co}_{11}$ phase can be described approximately as a B-centered periodic approximant. The relationship to the lattice parameters reported in literature and in the present work has been discussed.

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