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## **In-situ structural identification of $Zr_3Al_2$ type metastable phase during crystallization of a Zr-based MG**

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### **Abstract:**

A metastable phase was detected using higher energy synchrotron radiation when Zr-based metallic glass (MG) was annealed under vacuum in Linkam hot stage at 848 K. The formation and transformation processes of metastable phase were recorded by synchrotron radiation method. The metastable phase during crystallization was identified as  $Zr_3Al_2$  structure type according to powder diffraction and TEM analysis. The structure of  $Zr_3Al_2$  type MCP was experimentally evidenced by 3D diffraction patterns and mathematically described. The identification of  $Zr_3Al_2$  MCP could be helpful for the understanding of cluster structure of MG.

### **Key Words:**

metallic glass, metastable phase, crystallization, synchrotron radiation

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# 1 Introduction

Metallic glasses (MGs) have drawn great attention because of their unique liquid-like structure and the combination of superior properties, including high yield strength, good elasticity, good magnetic properties, high wear resistance and high corrosion resistance [1-3]. Upon heating, MGs undergo a series of thermal events including glass transition temperature ( $T_g$ ), supercooled liquid region ( $\Delta T_x$ ) and crystallization temperature ( $T_x$ ). In several MG systems, it has been reported previously that the crystallization process leads to the formation of distinctive metastable structures, such metastable crystalline phase (MCP) and metastable quasicrystal phase (MQC), as a result of nucleation of crystals from the non-equilibrium amorphous matrix [4-7]. Previous findings revealed the formation of MCP in  $Zr_{55}Al_{10}Ni_5Cu_{30}$  MG [6] and MQCs in  $Zr_{63}Cu_{25}Al_{12}$ ,  $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$  and  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloys during heating [8]. Subsequently, a number of studies were reported that MCPs or icosahedral MQCs were formed in different Zr-based MGs. For example, MQCs were found in Zr-based binary, ternary and multicomponent metallic glass formers with the addition of Ti, Pd or Pt [9-11]. Using fast quenching or ion irradiation methods [12, 13], MCPs or MQCs were also observed in metallic glassy matrix. When 1 wt.%  $La_2O_3$  was introduced into  $Zr_{55}Al_{10}Ni_5Cu_{30}$  alloy, MCP and MQC coexisted after thermal treatment [14]. Recent publications concerning metastable and quasicrystal phases formed in Zr-based glassy matrix are listed in table 1, which summarizes compositions or composition range of MCP/MQC formers, formation methods and the structure type of metastable phases.

In addition to alloy composition factor, oxygen impurity in the alloy, which can be introduced from raw materials or annealing environment, were also found to affect the nucleation process of

metastable phases in Zr-based alloys [30, 34]. When the content of oxygen reached 4.3 atomic percent (at.%) in  $Zr_{65}Cu_{27.5}Al_{7.5}$  ternary alloy, MQC had precipitated from glassy matrix [30]. However, when the content was lower than the critical value, another stable crystalline phase instead of MQC appeared. Similar experimental results were demonstrated in another study that high content of oxygen promoted the crystallization of metastable phase via the redistribution of oxygen [34]. Due to the different fabrication environment of MGs, the precipitation of MQCs in  $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$  and  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  MGs indicating low reproducible reliability which also can be interpreted by the different contents of oxygen. More recent researches interpreted the crystallization mechanisms in the point of view of thermodynamics and kinetics [37, 38].

In terms of MCP formation in MGs, the same one was found to have nucleated from the glassy matrix in annealed  $Zr_{55}Al_{10}Ni_5Cu_{30}$ ,  $Zr_{55}Cu_{20}Al_{10}Ni_{10}Pd_5$  and some other Zr-based MGs according to previous studies [15, 16]. The accurate identification of MCP structure is important because that it could be a strong evidence to interpret the configuration of clusters of metallic glasses. In order to clarify the structure of metastable crystalline phase of Zr-based MGs during crystallization,  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  MG was adopted in our work for further investigation. In this work, using high energy synchrotron radiation in transmission mode during in-situ heating and transmission electron microscopy (TEM), the structure of MCP nucleated in  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  metallic glass was identified and high temperature crystallization results were investigated.

## 2 Experimental

Master ingots of  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  (at.%) alloy were prepared by arc melting using high purity

metals, which were melted more than 3 times for homogeneity under the protection of high purity argon. Glassy ribbons were synthesized by melt spinning method. The ribbons were annealed under vacuum in a thermal treatment furnace at 848 K and 1073 K, respectively.

The as-spun ribbons without annealing were sealed under protection of argon flow in quartz capillaries and placed on a computer-controlled Linkam hot stage. The temperature was well controlled below the melting temperature of Zr-based alloy to prevent the reaction between Zr and Si of quartz crucible. The in-situ heating samples were examined using high energy synchrotron radiation in transmission on the ID11 beam line of the European Synchrotron Radiation Facilities (ESRF), which was monochromatized using a nitrogen-cooled double crystal silicon monochromator. The photon energy was 80 keV corresponding to an X-ray wave-length ( $\lambda$ ) of about 0.015498 nm. The diffraction spectra were acquired in transmission mode through the quartz capillary in the Linkam by a 2D CCD camera. The heating rate of the Linkam was 10 K/min. Acquisition and data processing times were configured as 20 seconds such that a full spectrum can be obtained.

The annealed samples were ground into the metallic powder. The powder was loaded into a thin glass capillary and mounted in a sample holder on the ID 31 high resolution powder diffractometer with the wave-length ( $\lambda$ ) of 0.050002 nm. The structure of the sample annealed at 848 K was investigated by TEM using selected area electron diffraction (SAED) with the wave-length ( $\lambda$ ) of 0.1542 nm.

### 3 Results and discussion

The X-ray diffraction patterns obtained under in-situ heating using synchrotron radiation in

transmission mode, the transition in detail from a metastable phase to stable ones, and the volume fractions of different nucleated crystalline phases as a function of temperature are shown in Fig. 1. In Fig. 1 a,  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloy exhibit fully amorphous microstructure evidenced by the absence of sharp Bragg peaks corresponding to crystalline structures, until the temperature reached  $T_x$  (~763 K). The phase initially nucleated from the amorphous alloy can be identified as a metastable phase. When the temperature went higher than 950 K, the peaks of the metastable crystalline phase was disappeared in Fig. 1 a. The phase transition from the metastable phase to stable ones can be clearly observed from Fig. 1 b, which is an enlarged view of Fig. 1 a. The diffraction peaks of disappearing metastable phase and emerging stable ones are marked in Fig. 1 b. The intensity of metastable phase was decreasing with the increase of temperature and the peaks disappear when the temperature reaches about 978 K. From Fig.1a and Fig1.1b, it appears that the strongest peak of the metastable phase has not vanished completely. However, the peak is shared by the bcc Zr phase, as are many similar peaks in the diffraction pattern.

The stable phases transform from metastable and the new crystalline particles significantly grow in the temperature region of that of diminishing of metastable phase. The volume of each

crystalline phase was normalized using the following formula:

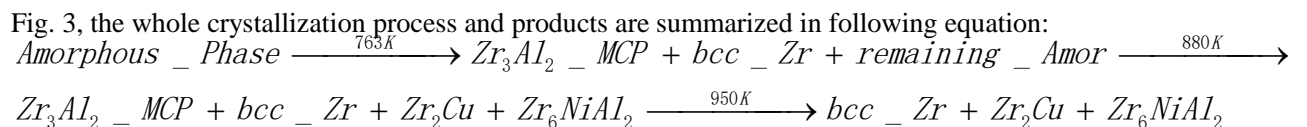
$$V_f = \frac{ph\_frac_i V_{uc_i}}{\sum_{i=1}^N ph\_frac_i V_{uc_i}} \quad (1)$$

where  $ph\_frac_i V_{uc_i}$  is the phase fraction of phase  $i$  and  $V_{uc_i}$  is the volume of the unit cell of that phase. In Fig. 1 c, the metastable phase (marked with solid triangle) nucleated at ~790 K, followed by bcc Zr (marked with cross). The volume fraction of MCP decreased from ~0.42 to 0 when the temperature went up from ~890 K to ~990 K. The stable phases including  $Zr_6NiAl_2$

(marked by solid square) and  $Zr_2Cu$  (marked with solid diamond) nucleated at about 850 K and 875 K, respectively.

Fig. 2 presents the diffraction pattern of annealed sample at 848 K (marked with black solid squares) using high energy powder X-ray diffractometer. In order to identify the structures of the crystalline phases, a thorough search of a database known as the Pauling Files [39] was made. The structures of all known binary combinations of the four elements zirconium, copper, nickel and aluminum were saved. The program “Powdercell” [40] was used to display the calculated diffraction patterns of these binaries. These are superimposed on top of the diffraction pattern from ID31. The calculated  $Zr_3Al_2$  and bcc Zr crystalline phase diffraction patterns match very well with the observed pattern of annealed  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloy. A  $Zr_3Al_2$  type structure can be identified for the metastable crystalline phase as marked with solid triangle. In the meantime, bcc Zr can also be observed with very similar diffraction peak positions to those of  $Zr_3Al_2$ .

When the temperature increased, the transformation from  $Zr_3Al_2$  MCP to stable phases occurred, as shown in Fig. 1. The crystalline phases annealed at 1073 K were identified using powder diffraction in ID31. The experimental diffraction patterns and the ones from database were compared in Fig 3. The annealed alloy is composed of multi-crystalline stable phases, which include bcc Zr,  $Zr_2Cu$  and ternary intermetallic  $Zr_6NiAl_2$ . In contrast, there is a complete absence of  $Zr_3Al_2$  structure type metastable phase in the XRD diffraction pattern. From Fig.1, Fig. 2 and



The  $Zr_3Al_2$  structure type metastable phase exhibits good thermal stability, which was observed in  $Zr_{55}Al_{10}Ni_5Cu_{30}$  and  $Zr_{55}Cu_{20}Al_{10}Ni_{10}Pd_5$  annealed alloys [15, 18]. The ratio of

transformation temperature over melting temperature is about 0.913. From previous results [15], the annealing temperature of  $Zr_3Al_2$  metastable phase is identified at nearly up to the melting point under fast heating rate. The difference in thermal stability of MCPs could be affected by heating rates and impurities. When the oxygen content goes up to 0.43 at.% [30], the formation of icosahedral quasicrystal phase nucleates instead of  $Zr_3Al_2$  structure type MCP. The variability of MCP and MQC can be interpreted by the affinity of Zr and O and when oxygen concentration reaches critical value. The formation of MCP and MQC was also found to be accompanied by the redistribution of oxygen [30, 34].

Using TEM and selected area electron diffraction (SAED), the structure of  $Zr_3Al_2$  structure type MCP was confirmed. Fig. 4 shows SAED patterns corresponding to three different crystallographic zone axes. The MCP is a tetragonal structured crystal with lattice parameters  $a = 7.88(\pm 0.08)$  Å and  $c = 7.10(\pm 0.08)$  Å. To visualize the crystal structure, the 3D crystal structure image was built and demonstrated in Fig. 5 using “Diamond” method [41]. The structure model is composed of large blue balls and small white ones, representing Zr/Ni/Cu and Al/Ni/Cu atoms, respectively. This means that Ni and Cu are capable of potentially occupying both ball positions. However, taking in to the consideration that the atomic percentage of Zr in  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  alloy and  $Zr_3Al_2$  MCP, and the atomic radii differences between Zr and M (Ni, Cu and Al), it is more probable that Zr atoms reside at the positions of blue balls and M (Ni, Cu and Al) occupy the positions of white balls. Therefore,  $Zr_3(Ni/Cu/Al)_2$  structure may be a reasonable structure of the metastable phase. As an intermediate stage between amorphous and  $Zr_2M$  ( $Zr_2Cu$  and  $Zr_6NiAl_2$ ) type stable phases, study on the  $Zr_3Al_2$  structure MCP with good thermal stability may benefit the understanding on the structure of multi-component Zr-based metallic glasses and their

devirtification behaviors.

In summary, the in-situ crystallization processes and the formation of metastable phase in  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  metallic glass with low content of oxygen were observed and analyzed using high energy synchrotron radiation. The metastable phase during crystallization was found and the structure of MCP was identified as  $Zr_3Al_2$  structure type according to powder diffraction and TEM analysis. The transition from  $Zr_3Al_2$  type MCP to  $Zr_2Cu$  and  $Zr_6NiAl_2$  was experimentally evidenced by 3D diffraction patterns and mathematically described using volume fraction function.

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Table 1

Table1 Metastable and quasicrystal phases in Zr-based metallic glasses

Alloys	Metastable phase	Method	References
Zr <sub>55</sub> Cu <sub>30</sub> Al <sub>10</sub> Ni <sub>5</sub>	MCP	annealing; ion irradiation	6, 14, 15, 16 12
Zr <sub>55</sub> Cu <sub>20</sub> Al <sub>10</sub> Ni <sub>10</sub> Pd <sub>5</sub>	MCP	annealing	18
Zr <sub>70</sub> Pd <sub>30</sub>	MQC	annealing	10, 19, 20, 21
Zr <sub>70</sub> Ni <sub>30-x</sub> Pd <sub>x</sub> , Zr <sub>70</sub> Cu <sub>30-x</sub> Pd <sub>x</sub> Zr <sub>70</sub> Ni <sub>10</sub> Cu <sub>10</sub> Pd <sub>10</sub> (x=10, 20 at.%)	MQC	annealing	10
Zr <sub>55</sub> Ti <sub>4</sub> Cu <sub>25</sub> Al <sub>10</sub> Cu <sub>16</sub>	MCP	annealing	15, 16
Zr <sub>69.5</sub> Cu <sub>12</sub> Ni <sub>11</sub> Al <sub>7.5</sub>	MCP MQC	annealing	15, 16, <i>this work</i> 8
Zr <sub>65</sub> Pd <sub>10</sub> Al <sub>7.5</sub> Ni <sub>10</sub> Cu <sub>7.5</sub>	MQC	annealing	16
Zr <sub>2</sub> Cu <sub>0.5</sub> Pd <sub>0.5</sub>	MQC (C16)	annealing	22
Zr <sub>65</sub> Al <sub>7.5</sub> Ni <sub>5</sub> Cu <sub>17.5</sub> Re <sub>5</sub>	MQC	annealing	23
Zr <sub>63.33</sub> Ti <sub>8.89</sub> Cu <sub>15.45</sub> Ni <sub>12.33</sub>	MQC	annealing	24
Zr <sub>62-x</sub> Ti <sub>x</sub> Cu <sub>20</sub> Ni <sub>8</sub> Al <sub>10</sub> (2≤x<4)	MQC	annealing	9
Zr <sub>65</sub> Pd <sub>35</sub> , Zr <sub>80</sub> Pt <sub>20</sub>	MQC	annealing cooling	19, 21
Zr <sub>70</sub> Cu <sub>20</sub> Ir <sub>10</sub> , Zr <sub>70</sub> Cu <sub>20</sub> Rh <sub>10</sub>	MCP (Ti <sub>2</sub> Ni type)	annealing	25
Zr <sub>y</sub> (Ti <sub>0.186</sub> Nb <sub>0.058</sub> Cu <sub>0.324</sub> Ni <sub>0.258</sub> Al <sub>0.174</sub> ) <sub>100-y</sub> (y=57 and 62)	MQC	annealing	26
Zr <sub>65</sub> Al <sub>7.5</sub> Ni <sub>5</sub> Cu <sub>17.5</sub> Zn <sub>5</sub>	MQC	annealing	27
Zr <sub>66.7</sub> Pd <sub>33.3</sub>	MQC	annealing	28

$Zr_{52.5}Hf_2Ti_{7.5}Cu_{20}Al_{10}Ni_8$	MCP (Ti <sub>2</sub> Ni-type)	annealing	17, 29
$Zr_{75}Pt_{25}, Zr_{77}Pt_{23}$	MQC	annealing	11
$Zr_{65-x}Cu_{27.5}Al_{7.5}O_x$ (x=0.43% and 0.82%)	MQC	annealing	30
$(Zr_{0.51}Cu_{0.207}Ni_{0.12}Al_{0.163})_{99.5}Y_{0.5}$	MCP (orthorhombic)	annealing	31
$Zr_{65}Ni_{17.5}Ni_{10}Al_{7.5}$	MQC	annealing	8
$Zr_{70}Ni_{23}Ti_7$	MQC	annealing	32
$Zr_{67}Ni_{33}, Zr_{58}Ni_{42}$	MCP	annealing	33
$Zr_{65}Cr_{15}Al_{10}Pd_{10}$	MCP (O-rich)	annealing	34
$(Zr_{65}Al_{7.5}Cu_{27.5})_{100-x}Ti_x$ (x=2-15 at.%)	MQC	annealing	13
$(Zr_{65}Al_{7.5}Cu_{27.5})_{90}Ti_{10}$		as cast	
$Zr_{55}Al_{10}Ni_5Cu_{30}$ +1 wt.% La <sub>2</sub> O <sub>3</sub>	MCP+MQC	annealing	14
$Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$	MQC	annealing	35
$(Zr_{0.58}Nb_{0.03}Cu_{0.16}Ni_{0.13}Al_{0.1})_{98.5}Y_{1.5}$	MQC	annealing	36

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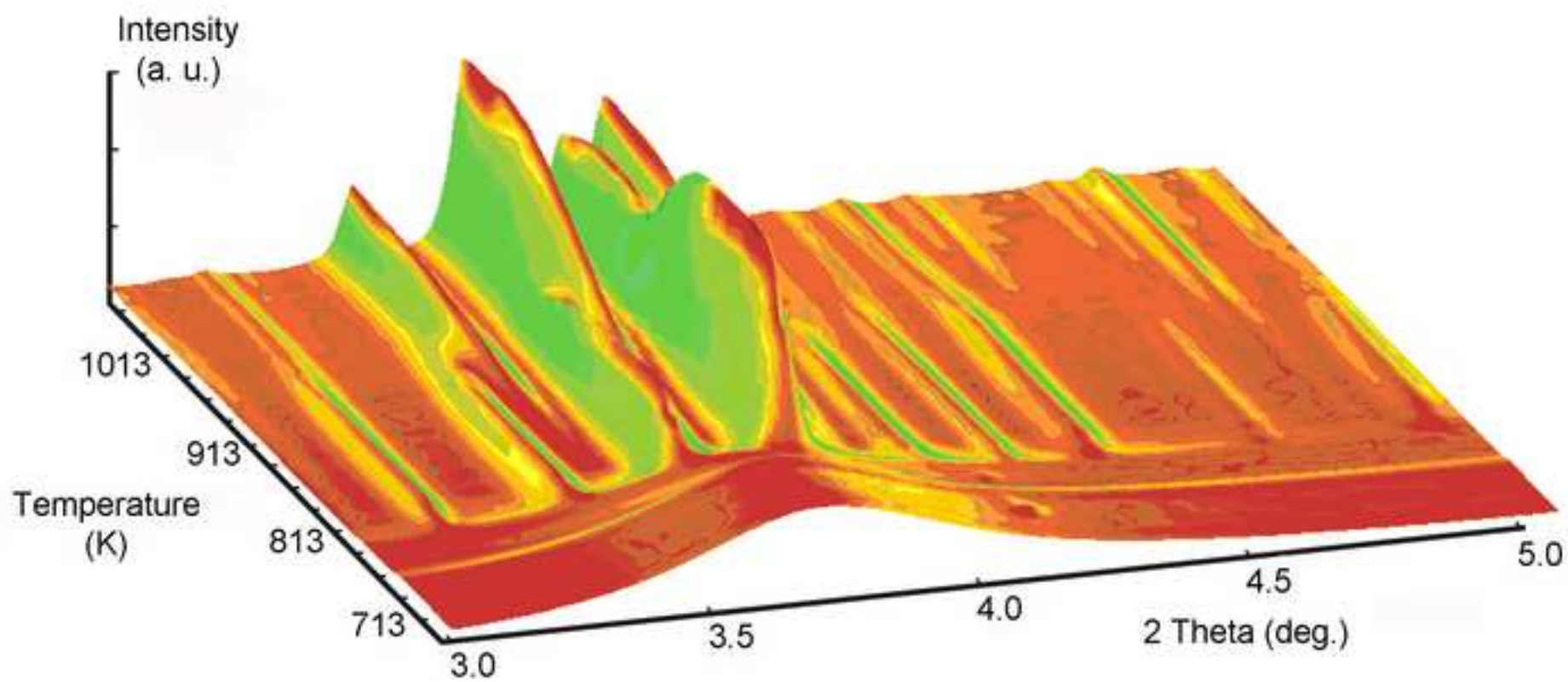
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Fig. 5 Crystal structure of  $Zr_3Al_2$  structure type MCP, image created using “Diamond”.



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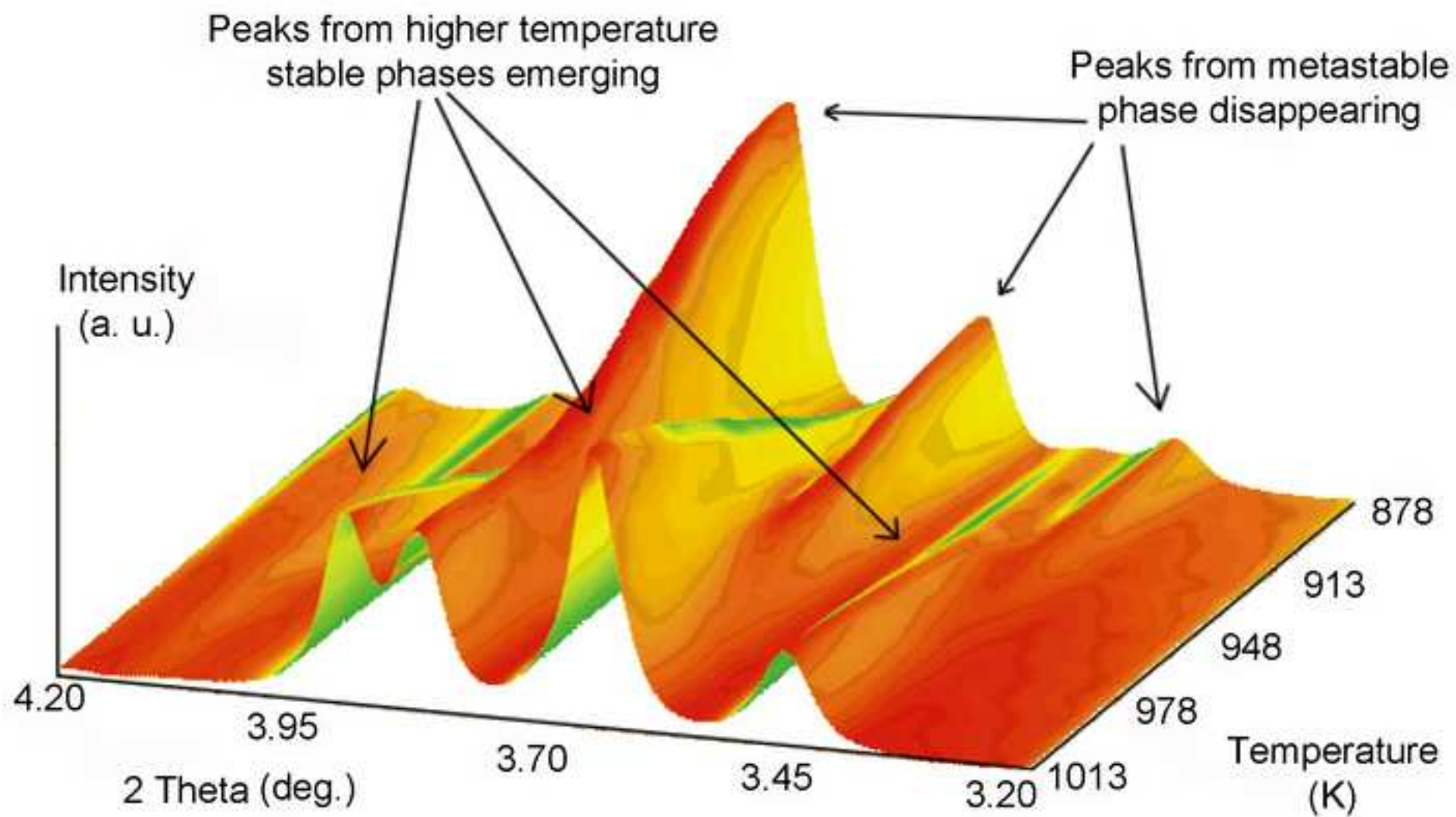


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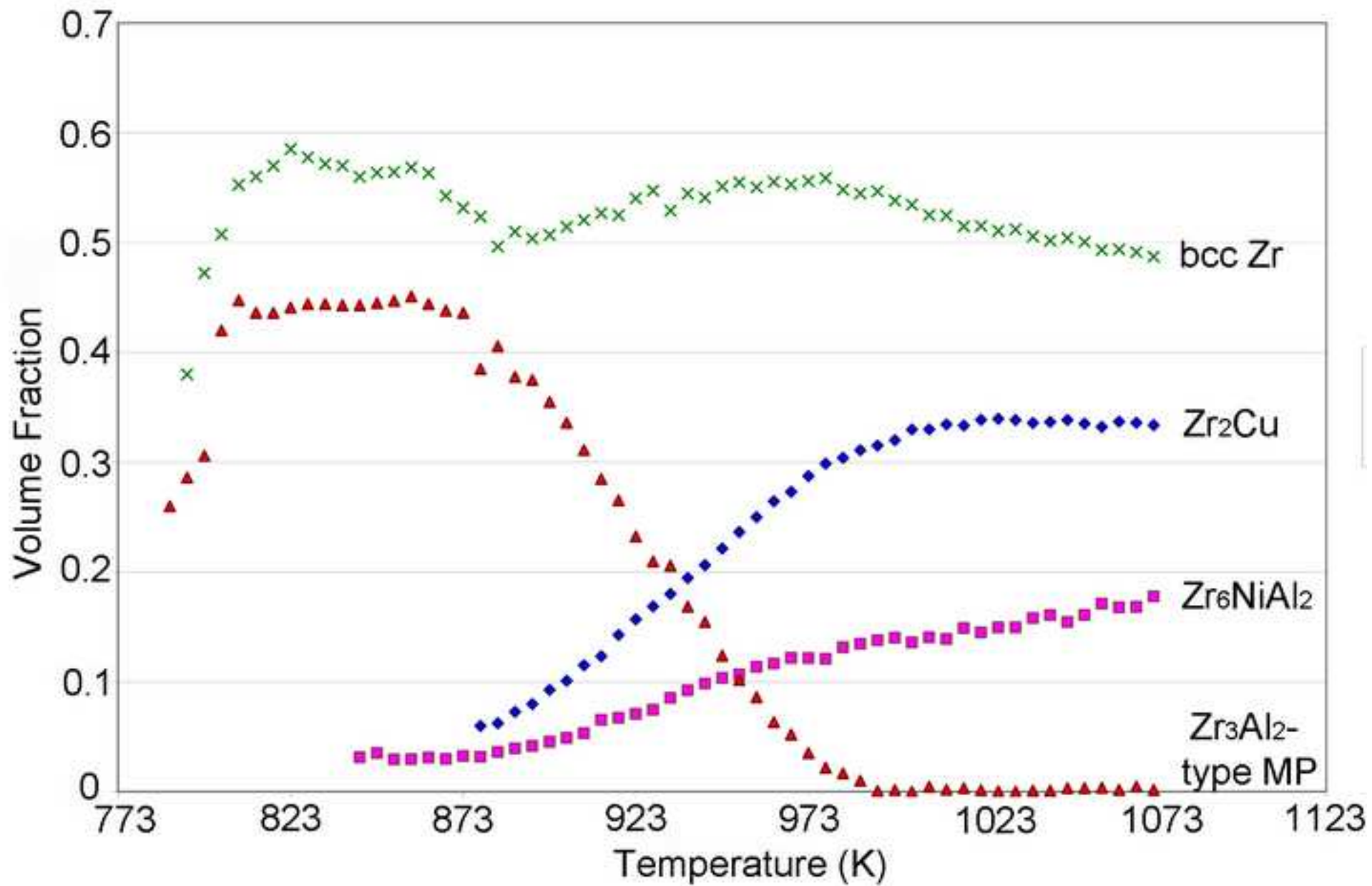
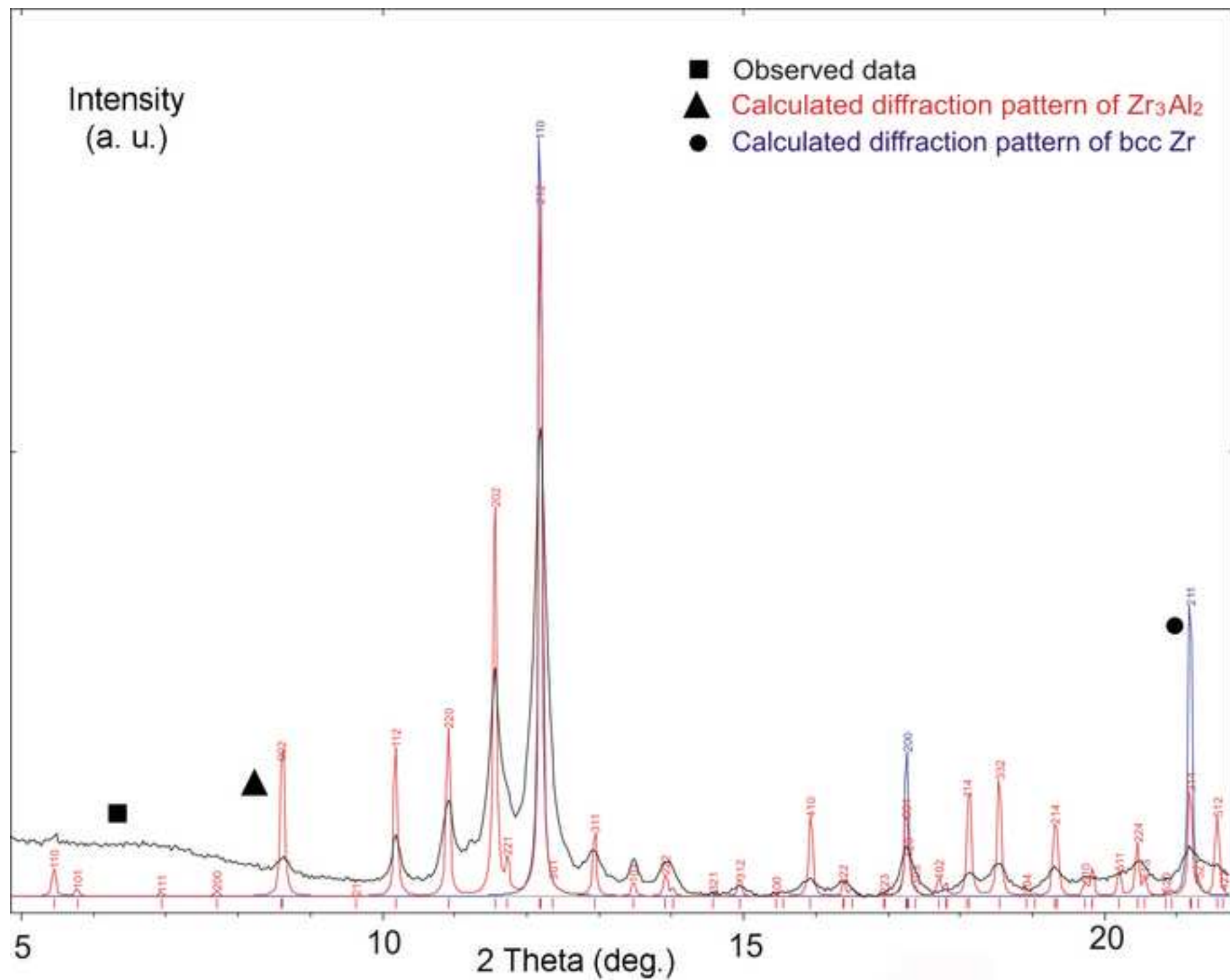
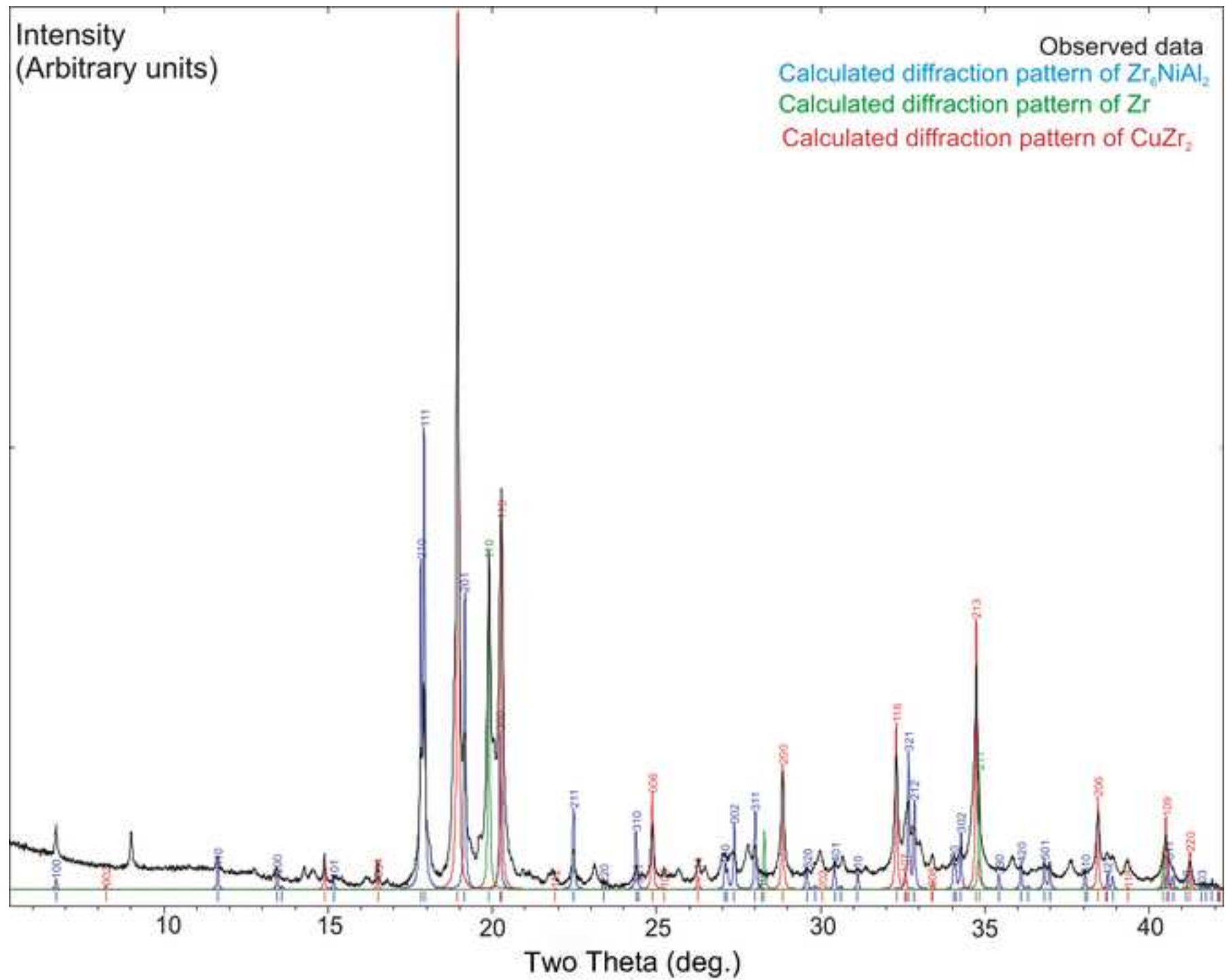


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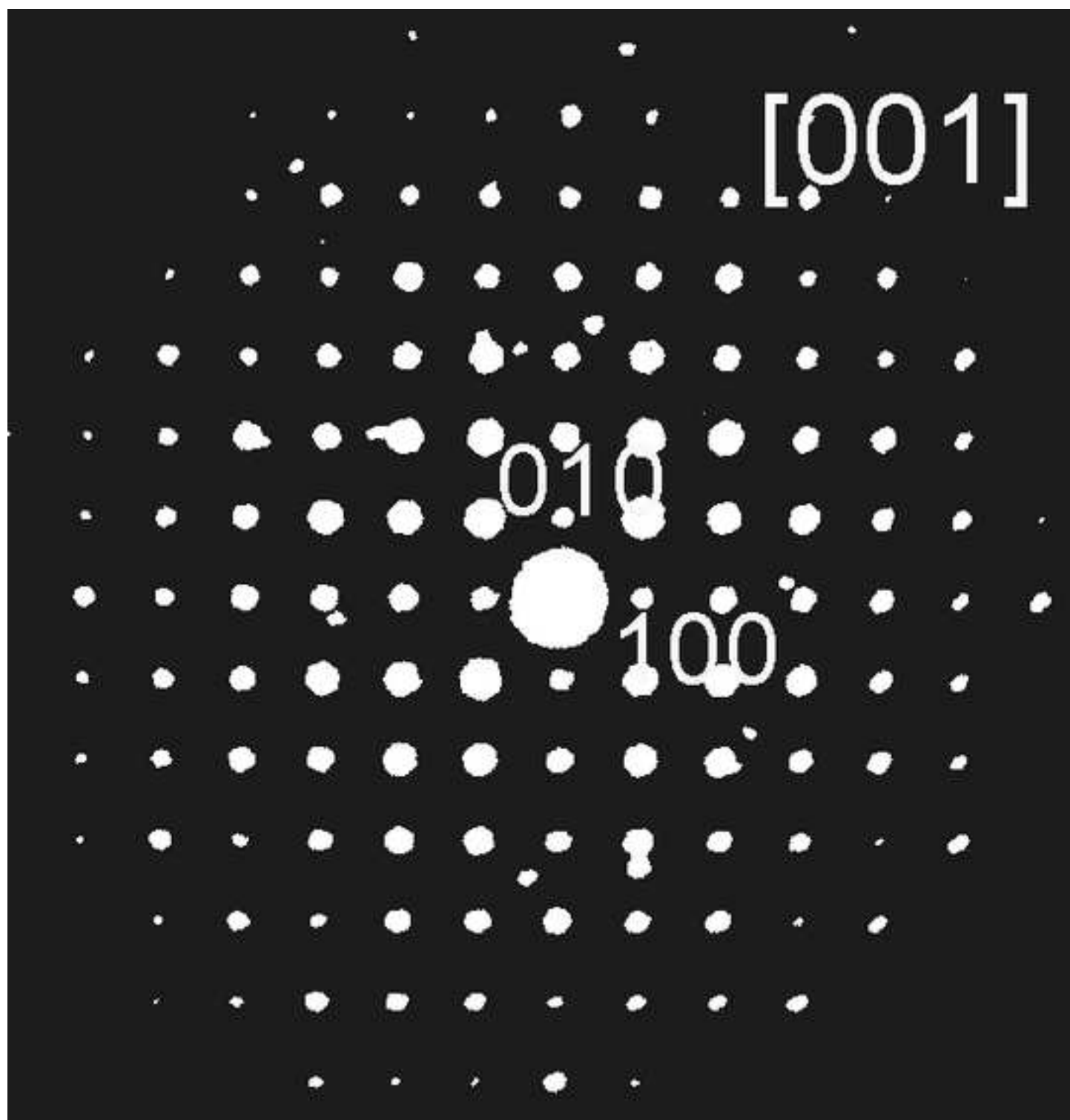
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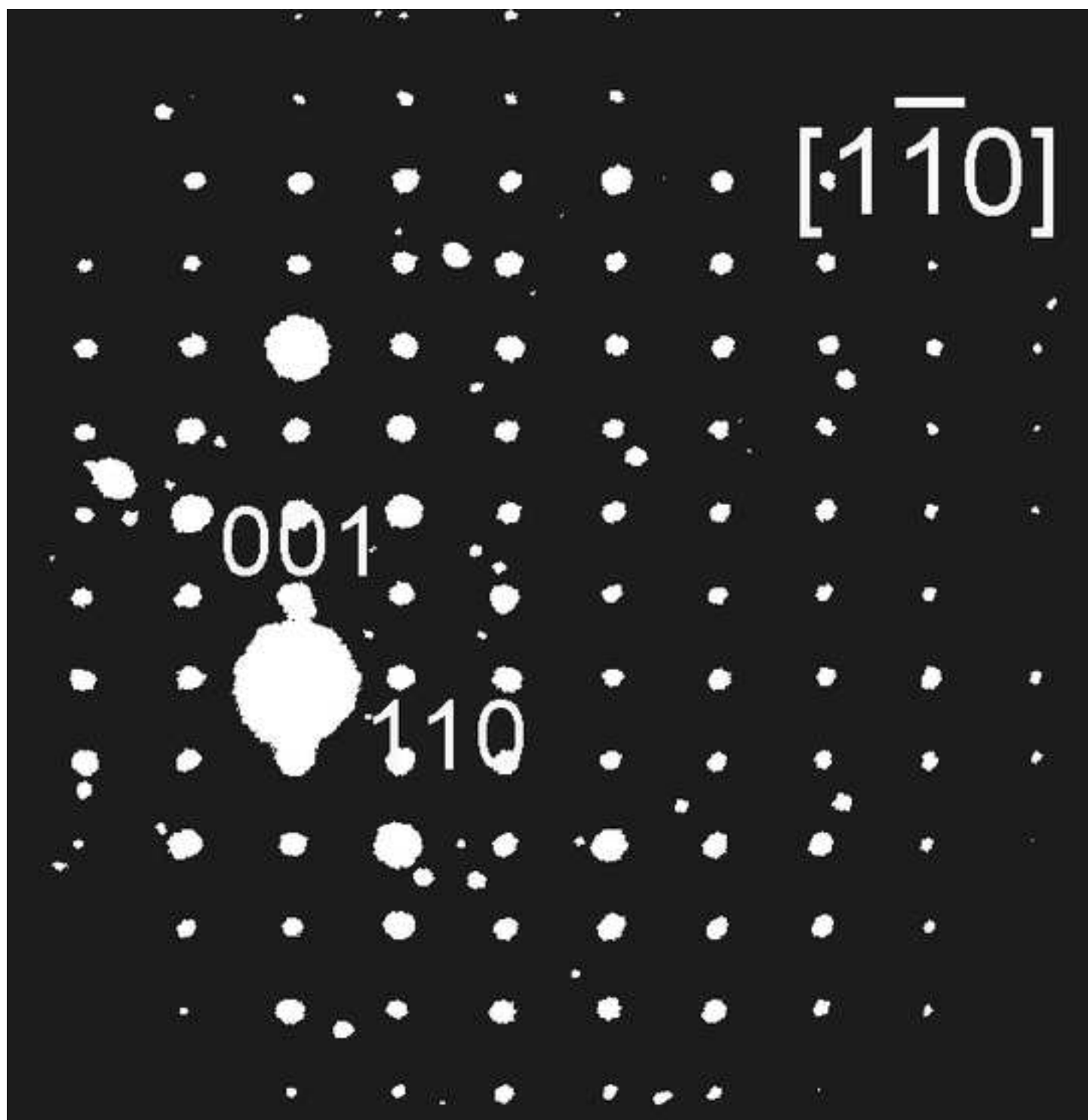
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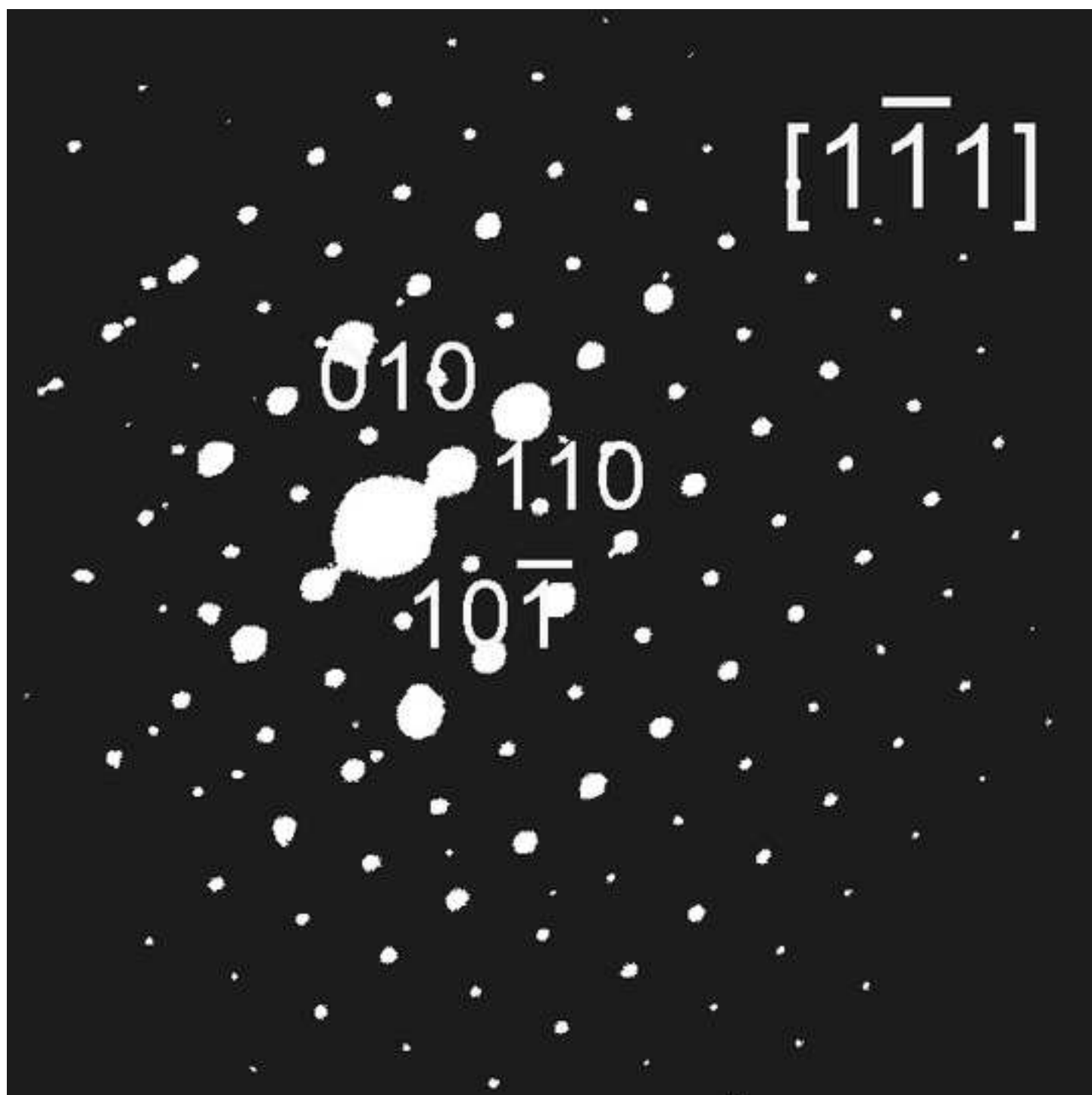




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