TWINNING MECHANISM IN PrCo$_2$C$_x$ MAGNETIC PHASE

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ABSTRACT

A magnetic rhombohedral PrCo$_2$C$_x$ ($x$=0.05–0.25) phase (space group $R\overline{3}m$), which is heavily twinned along the {110} and {211} planes, was identified. The twinning mechanism was explored by analyzing the reduction of crystal symmetry due to the cubic-rhombohedral phase transformation. The origin of the twinning and the formation of four twin variants were attributed to the insertion of carbon interstitials into Co$_4$ tetrahedrons along the $\bar{3}$ axis in the rhombohedral lattice, which corresponds to one of the four equivalent <111> axes of its parent PrCo$_2$ cubic-lattice.

INTRODUCTION

Recently, rare-earth-cobalt (RE-Co) permanent magnets have attracted considerable scientific and technical interest, primarily because of their high Curie temperatures and high magnetocrystalline anisotropy [2]. Fuerst and his co-workers [3,4,5] reported that the remanence of PrCo$_5$-based magnets can be enhanced by thermal mechanical alignment or die-upsetting treatment, which was originally developed for melt-spun Nd$_2$Fe$_{14}$B alloys [6]. They also found that coercivity can be improved by adding or substituting elements into the alloy [4]. While adding a high concentration of carbon significantly decreases remanence, low levels of carbon actually increased coercivity and remanence compared with the carbon-free alloy. Among the PrCo$_5$-based magnets studied, Pr$_{18}$Co$_{82-y}$C$_y$ ($0.5 \leq y \leq 1$) had superior coercivities and energy products.

During investigations of origin of the enhanced coercivities in die-upset Pr-Co magnets [7], we studied the microstructures of a series of samples Pr$_{18}$Co$_{82-y}$C$_y$ ($0 \leq y \leq 6$), focusing on the location of the carbon atoms and the changes in crystal structure. In Pr$_{18}$Co$_{81}$C, which has the optimum carbon concentration and best magnetic properties in the series, two major phases co-exist, hexagonal PrCo$_5$ and cubic PrCo$_2$, both of which are magnetic [8]. Energy dispersive x-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) analyses showed that carbon only goes into the heavily twinned PrCo$_2$ phase, in contrast to the untwinned PrCo$_2$ in carbon-free Pr$_{18}$Co$_{82}$. This finding suggested that carbon doping resulted in a diffusionless structural transformation. In this article, we report our observations and interpretation of the carbon-doping-related twinning from detailed crystallographic analyses to shed light on the structural origin of such a transformation in this permanent magnetic compound.

TWINNING STRUCTURE AND CRYSTALLOGRAPHY

Extensive transmission electron microscope (TEM) investigations using imaging, diffraction, EDS, and EELS showed that Pr$_{18}$Co$_{81}$C is composed of carbon-free PrCo$_5$ and carbon containing PrCo$_2$. The carbon concentration of the heavily twinned PrCo$_2$ phase depends on grain and area, varying from $x$=0.05 to $x$=0.25 (hereafter, we denote this phase as PrCo$_2$)$_x$, $x$=0.05 - 0.25). Fig.1 shows the typical morphology of the primary twins and secondary twins. The crystal structure of the PrCo$_2$C$_x$ phase differs greatly from the face-centered cubic PrCo$_2$ (space group Fd$\overline{3}$m, $a$=0.73nm). By systematically tilting the crystal to various zone-axes about several major diffraction rows, we determined it to be a rhombohedral phase with space group $R\overline{3}$m and lattice parameters $a$=0.522nm $\alpha$=62.5° (equivalent to a hexagonal lattice with $a$=0.542nm and $c$=1.254nm). Table I lists its Wyckoff positions.
A major feature of the diffraction patterns in the PrCo$_2$C$_x$ phase is that the Bragg spots split along the [110]$^*$ or [211]$^*$ direction, and the splitting increases with distance from the [110]$^*$ or [211]$^*$ row, as seen in Fig. 2(a) and (b) where the subscripts M and T denote the matrix and twin, respectively. The diffraction patterns are very similar to those observed in YBa$_2$Cu$_3$O$_{7.8}$ [9], suggesting they are reflection twins with the (110) or (211) plane as their twinning planes. For both the (110) and (211) twins, the $\alpha$ angle of rhombohedral lattice (or the splitting of the Bragg spots) varies with carbon concentration. The angle can differ from 60.5° to 63° for carbon concentrations $x=0.05 - 0.25$. Fig. 2(b) shows two diffraction patterns of the [124] zone axis for $x=0.2$ ($\alpha=62.5°$) (upper pattern) and $x=0.05$ ($\alpha=60.5°$) (lower pattern). The lattice parameter $a$ shows a slight but not significant ($<0.01$ nm) increase with carbon concentration.

In addition to (110) and (211) primary twins, we often observed secondary twins: (110)(211) [(211) twinning in (110) twin lamellas], as shown in Fig. 1(b) and (c). Fig. 2(c) is the corresponding electron diffraction pattern taken along the [110] direction. Both morphology and selected-area diffraction pattern showed that there are four twin variants, M, T$_1$, T$_2$, and T$_3$ (also denoted as $V_i$ (i=1,2,3,4) in Fig. 1(c)). For reflection twin, the twinning crystallography can be mathematically expressed as [10]:

$$A_T = T_{hkl} A_r,$$

$$T_{mT} = I - 2 \frac{H\bar{U}}{UH},$$

where $A$ and $A_T$ are the column matrix of the basic axes of matrix and twin, respectively, $T_{hkl}$ is a twinning matrix of (hkl) twins, I is an identity matrix, $H$ is the column matrix of the twinning plane (hkl) and $\bar{U}$ is the row matrix of the twinning plane normal [uvw] ([hkl]* // [uvw]). For

<table>
<thead>
<tr>
<th>Wyckoff Positions</th>
<th>Atoms</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>2c</td>
<td>Pr</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>1.0</td>
</tr>
<tr>
<td>3e</td>
<td>Co</td>
<td>0.500</td>
<td>0.500</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>1b</td>
<td>Co</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
<td>0.6</td>
</tr>
<tr>
<td>2c</td>
<td>Co</td>
<td>0.540</td>
<td>0.540</td>
<td>0.540</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.392</td>
<td>0.392</td>
<td>0.392</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table I Wyckoff positions of the PrCo$_2$C$_x$ phase (Space group R$\overline{3}$m)
Figure 2 Electron diffraction patterns of PrCo$_x$C$_y$ phase: (a) [110] pattern with (110) primary twins; (b) [124] pattern with (211) primary twins; (c) [110] pattern with (110)(211) secondary twins.

(110)(211) secondary twinning, the sequence can be written as:

\[
\begin{align*}
M & \rightarrow (110) \rightarrow T_1 \rightarrow (211)T_1 \rightarrow T_2 \rightarrow (101)T_2 \rightarrow T_3 \rightarrow (211)T_3 \rightarrow M
\end{align*}
\]

where $A_{T_i}$ is the column matrix of the basic axes of the $T_i$ (i = 1, 2, 3) lattice. Since the (110) and (211) lattice planes are not parallel, only when the [111] axis of the crystal is parallel to the incident beam can both the primary and secondary twins be viewed edge-on (Fig. 1(b)). In the [110] orientation, the (110) twins are viewed edge-on, while the (211) twins are viewed inclined, showing thickness fringes (Fig. 1(c)). Although there are four twin variants in Fig. 2(c), only three sets of Bragg spots are visible in the [110] diffraction pattern (Fig. 2(c)) because the superimposition of the diffraction patterns of the zero-order Laue zone of the $T_2$ and $T_3$ lattices. In this [110] zone axis, $M$ and $T_1$ are in exact zone orientation, but there is an in-plane rotation ($\varphi = 6.1^\circ$) due to the twinning. [010]$_{T_2}$ is parallel to [010]$_{T_3}$, while [010]$_{T_2}$ and [010]$_{T_3}$ deviate 2.1° from [110]$_M$. The Bragg spots of $T_2$ and $T_3$ are also split 6.1° due to the twinning in the high-order Laue zones.

**THE ORIGIN OF THE TWINNING**

Because PrCo$_2$ is an untwinned phase, the formation of a twin in PrCo$_3$C$_x$ apparently is driven by a minimization in lattice strain caused by adding carbon atoms, which also is the origin of the cubic-rhombohedral phase-transformation. Thus, the twinning mechanism can be addressed by the structural transition of PrCo$_2$ (space group Fd3m) to PrCo$_3$C$_x$ (space group R3m). A rhombohedral lattice can be derived from a face-centered cubic lattice by axial transformation, as shown in Fig. 3(a). In the rhombohedral unit-cell, there is a pair of two face-shared tetrahedrons (PrCo$_3$ and Co$_4$) which provide interstitial sites for carbon at 2c Wyckoff positions ($x$, $x$, $x$) in the rhombohedral cell (see also Table I). Although the size of the interstitial space in the PrCo$_3$ tetrahedron is similar to that in the Co$_4$ tetrahedron, the latter can be easily expanded by displacing along the [111] direction the apex Co atom that is at the body-center site. In contrast, the apex Pr atom of the PrCo$_3$ tetrahedron cannot move because the neighboring Pr atom is very near to it along the [111] direction. The shift of the apex Co atom of the Co$_4$ from the body-center position is evidenced by our analysis of the extinction rules of the Bragg
reflections of the crystal, since the occupancy of the body-center position causes the extinction of the 110 reflection, i.e., the structure factor \( F_{110} = 0 \). However, this is not the case for \( \text{PrCo}_2\text{C}_x \), as the 110 reflection is clearly visible. The presence of the 110 reflection in Fig. 2(a) cannot be generated by double diffraction. Kinematical calculation of the intensity of the 110 reflection suggests that the Co atom shifts by about 0.2 nm from the body-center site.

Based on our diffraction analysis, we conclude that carbon goes into \( \text{Co}_4 \) tetrahedrons but not into \( \text{PrCo}_3 \). Because of the shift of the Co atom from the body-center position, after one carbon occupies the center of the \( \text{Co}_4 \) tetrahedron, the size of the interstitials in the neighboring \( \text{Co}_4 \) tetrahedron is reduced so it cannot accept another carbon (Fig. 3(c)). This suggests that one rhombohedral unit-cell cannot accept more than one carbon, consistent with our EDS analysis. The lower the carbon concentration is, the smaller is the \( \alpha \). The average corresponding lattice parameters of the \( \text{PrCo}_2\text{C}_x \) phase are \( \alpha = 62.5^\circ \) and \( a = 0.522 \) nm, which corresponds to one carbon in 2–3 rhombohedral unit cells (\( x = 0.2 \)).

Inserting carbon into \( \text{Co}_4 \) tetrahedrons changes the rhombohedral angle \( \alpha \) from 60° to about 62.5° (corresponding to the change of axial angles of the cubic lattice from 90° to 92.1°). We note that among four equivalent \(<111>\) axes in the cubic lattice, only one of them, say \([\overline{1}11]\), along which the carbon is inserted retains a \( \overline{3} \) symmetry (corresponding to the \([111]\) axis of the rhombohedral lattice) with three mirrors parallel to it; all the other \(<111>\) axes do not have \( \overline{3} \) symmetry. In other words, upon structural transformation, the parent phase \( \text{PrCo}_2 \) (space group \( \text{Fd}\overline{3}m \)) loses its three \( \overline{3}<111>\) axes and three \( 4<001>\) axes, and degenerates into a new phase with a space group of \( \text{R}\overline{3}m \), a subgroup of \( \text{Fd}\overline{3}m \). If we consider the carbon in the crystal matrix (denoted as original variant \( V_1 \)) is inserted along the \([\overline{1}11]\) axis, then for a neighboring area with carbon insertion along the \([111]\) axis, the variant \( V_2 \) formed at this area is related to the \( V_1 \) by \( m(110) \) symmetry operations (Fig. 4(a)). This suggests that \( V_2 \) and \( V_1 \) have a twinning relation with the \((110)\) plane as their twinning planes. The \((211)\) reflection twinning can be derived similarly (Fig. 4(b)). Table II lists the twinning relation for carbon inserting along different \( <111>\) directions.

**GROUP-THEORETICAL CONSIDERATION**

Twinning also can be considered using group theory on domain formation during disorder-order structural transformation [11], since different orientation variants of the ordered phase have an equal probability of being generated if their structures are related by a symmetry operation of the disordered parent phase. The ordering is usually accompanied by a decrease in symmetry...
The relation between the insertion direction of the carbon interstitial and the twinning plane.

<table>
<thead>
<tr>
<th>Axis*</th>
<th>Twinning plane**</th>
<th>Twinning variant</th>
</tr>
</thead>
<tbody>
<tr>
<td>[111]</td>
<td>(110)</td>
<td>V_2</td>
</tr>
<tr>
<td>[111]</td>
<td>(112)</td>
<td></td>
</tr>
<tr>
<td>[111]</td>
<td>(101)</td>
<td>V_3</td>
</tr>
<tr>
<td>[111]</td>
<td>(121)</td>
<td></td>
</tr>
<tr>
<td>[111]</td>
<td>(011)</td>
<td>V_4</td>
</tr>
<tr>
<td>[111]</td>
<td>(211)</td>
<td></td>
</tr>
</tbody>
</table>

* in PrCo_2 cubic coordinate.  
** in PrCo_2C_r rhombohedral coordinate.  

We considered that carbon insertion along the [111] or [111] axis forms an original variant \( V_1 \).

in such a way that the point group of the ordered structure \( H \) of order \( q \) is a subgroup of the disordered structure \( G \) of order \( p \) (\( H \subseteq G \)), and the number of orientation variants is equal to the order of the point group of the disordered phase divided by that of the ordered phase, i.e., \( p/q \). In our case, the disordered structure is \( \text{PrCo}_2 \) with \( G = m\overline{3}m, p = 48 \), while the ordered structure is \( \text{PrCo}_2C_r \) with \( H = \overline{3}m \) and \( q = 12 \). Thus, \( \text{PrCo}_2C_r \) has four orientation variants, since \( p/q = 4 \). We denote the variants as \( V_i \) (i=1,2,3,4) and their point group as \( H \). We can decompose \( G \) into cosets of \( H \) with the number of cosets equal to \( p/q \):

\[
G = g_1H + g_2H + g_3H + g_4H
\]

where \( g_i \) are elements of \( G \), \( g_i \in G \) (i=1,2,3,4), \( g_1 = E \) (\( E \) is an identity operation), and \( g_i \in H \) (i=2,3,4). For convenience, we assigned \( m[100], m[010], \) and \( m[001] \) to \( g_2, g_3, \) and \( g_4, \) respectively, to obtain all possible symmetry operations for coset \( g_iH \). Table III shows that for each coset \( g_iH \) there are 12 equivalent operations, any of which can change the original orientation variant \( V_1 \) to a new variant \( V_i \) (i=2,3,4). For example, in coset \( g_2H \), any of the 12 symmetry operations (listed in the same row as \( g_2H \) in Table III), such as \( m[100] \) and \( 2[100] \), can change \( V_1 \) to \( V_2 \). Using the crystallographic relation between the cubic and rhombohedral lattice and ignoring the small deviation from an \( \alpha \) value of exactly 60° in the rhombohedral lattice, we

![Figure 4](image_url)  

Figure 4 (a) (110) twinning; (b) (211) twinning and the four orientation variants \( V_i \) (i=1,2,3,4) (only two cell of the variants with the (211) twinning relation are depicted). The symbol \( * \) denotes the twin, and the subscripts c and r denote the cubic and rhombohedral lattices, respectively. The open arrows denote the \( \overline{3} \) axial direction of the twin variants.
### Table III The symmetry operations of cosets and the corresponding twinning *

<table>
<thead>
<tr>
<th>g₁H (g₁=E')</th>
<th>T</th>
<th>m[110]</th>
<th>m[101]</th>
<th>m[011]</th>
<th>3'[111]</th>
<th>3'[111]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g₂H (g₂=m[100])</td>
<td>m[100]</td>
<td>4'[001]</td>
<td>4'[010]</td>
<td>m[011]</td>
<td>3'[111]</td>
<td>3'[111]</td>
</tr>
<tr>
<td>Twinning</td>
<td>(110)</td>
<td>(101)(211)</td>
<td>(011)(121)</td>
<td>(112)</td>
<td>(121)(112)</td>
<td>(211)(112)</td>
</tr>
<tr>
<td>g₃H (g₃=m[010])</td>
<td>m[010]</td>
<td>4'[001]</td>
<td>m[101]</td>
<td>4'[010]</td>
<td>3[111]</td>
<td>3'[111]</td>
</tr>
<tr>
<td>Twinning</td>
<td>(101)</td>
<td>(110)(211)</td>
<td>(121)</td>
<td>(011)(121)</td>
<td>(211)(121)</td>
<td>(112)(121)</td>
</tr>
<tr>
<td>g₄H (g₄=m[001])</td>
<td>m[001]</td>
<td>m[110]</td>
<td>4'[010]</td>
<td>4'[010]</td>
<td>3'[111]</td>
<td>3'[111]</td>
</tr>
</tbody>
</table>

* The four rows in the table correspond to four twin variants Vᵢ (i=1,2,3,4). The brackets represent symmetry operations in a cubic notation, and the parentheses represent twinning in a rhombohedral notation.

derive that both operations of m[100] and 2[100] (cubic notation) are equivalent to the operation of the (110) reflection twinning (rhombohedral notation). The (110) primary twinning or the other twinning operations listed in the same line correspond to the same orientational geometry and give rise to the same twin variant V₂. In the same way, the orientation variants V₃ and V₄ can be generated by the operations listed in rows g₃H and g₄H, respectively. The four twinning variants Vᵢ (i=1,2,3,4) are depicted in Fig.4(b).

### CONCLUSIONS

The origin of the twinning can be attributed to the insertion of carbon atoms into one of the two Co₄ tetrahedrons in the PrCo₂Cₓ (x=0.05-0.25) unit-cell, which also causes a cubic to rhombohedral phase-transformation. The crystallographic relation of both primary twins ({110} and {211} twins) and secondary twins ({110} {211} twins) was analyzed using group theory, and was consistent with a structural model involving carbon interstitials in the Co₄ tetrahedrons along four equivalent <111> axes in the original PrCo₂ cubic crystals [12].

### REFERENCES

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