Microstructural analysis of twinned β-$Gd_5Si_2Ge_2$

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The room-temperature microstructure of the giant magnetocaloric material $Gd_5Si_2Ge_2$ is investigated using transmission electron microscopy and selected area diffraction. Nonmerohedral twinning is identified and its twin law, which relates one twin component to the other, is revealed. Based on selected area diffraction pattern data, we build a structural model for nonmerohedral twinning and explain its origin in terms of the irregular shear movement of two-dimensional $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs held together by (Si,Ge) dimers.

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The material $Gd_5Si_2Ge_2$ is of great interest not only because it shows an unprecedented giant magnetocaloric effect,[1–3] which could be used in near-room temperature magnetic refrigeration,[4] but it also exhibits a remarkable structural transformation from low-temperature orthorhombic (α-$Gd_5Si_2Ge_2$) to high-temperature monoclinic symmetry (β-$Gd_5Si_2Ge_2$) in the temperature range 276–330 K under magnetic field, 0–15 T, respectively.[1–3,5,6] In the course of the $\alpha \rightarrow \beta$ phase transition, 25% of the (Si,Ge)-(Si,Ge) dimers that exist in the α structure break their covalent bonds, resulting in isolated Si and/or Ge atoms. Furthermore, this breaking and forming of covalently bonded dimers can be repeated by cycling across the transition temperature.[6] This extraordinary phenomenon stems from unique structural motifs found in $Gd_5Si_2Ge_2$.

The structures of α- and β-$Gd_5Si_2Ge_2$ can be constructed from $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs held together by (Si,Ge) dimers [see Fig. 1(a)]. Upon the $\alpha \rightarrow \beta$ phase transformation, these slabs undergo a shear movement along the crystallographic **a** direction in the orthorhombic α phase, which breaks one-half of the (Si,Ge)-(Si,Ge) covalent bonds between the slabs, and becomes the monoclinic β phase, as shown in Fig. 1(b). Studies on other compositions, $Gd_5(Si_xGe_{1-x})_4$, and different $Ln_5(Si_xGe_{1-x})_4$ systems (Ln=lanthanide) indicate that the $^{\infty}_{2}[Ln_5(Si_xGe_{1-x})_4]$ slabs are the basic units undergoing shear movements, and also play a pivotal role in the giant magnetocaloric effects of these systems.[7,8]

Another interesting structural feature in β-$Gd_5Si_2Ge_2$ is nonmerohedral twinning,[6,9–12] for which only a small portion of reflections from two twin components are exactly superimposed while the remaining reflections are not. The nonmerohedral twinning in β-$Gd_5Si_2Ge_2$ vanishes and reappears, respectively, as the material is cycled across the transition temperature.[6] In this paper, we present analysis of the twinned structure of β-$Gd_5Si_2Ge_2$ using transmission electron microscopy (TEM) and selected area diffraction (SAD).

The $Gd_5Si_2Ge_2$ sample examined in this study was prepared by arc melting its constituent elements (purity; Gd, 99.8%; Si, 99.99%; Ge, 99.99%, based on atoms) in an argon atmosphere on a water-cooled copper hearth. The resulting button was remelted several times to ensure homogeneity, and then annealed at 1570 K for 1 h. Scanning electron microscopy (SEM) was used to ensure that the microstructure was homogeneous. The sample was mechanically thinned to 140 μm, reinforced with epoxy and a single slit Mo support grid and then mechanically dimpled until the center was perforated. During the dimpling process the sample was again reinforced with epoxy after cracks started to appear. The sample was ion milled at 4.5 kV, 15°, and 1 mA for 1.5 h, to clean the surface. TEM bright field (BF) images and SAD patterns were taken of the sample both off and on zone axes.

SEM examination of $Gd_5Si_2Ge_2$ shows no indication of

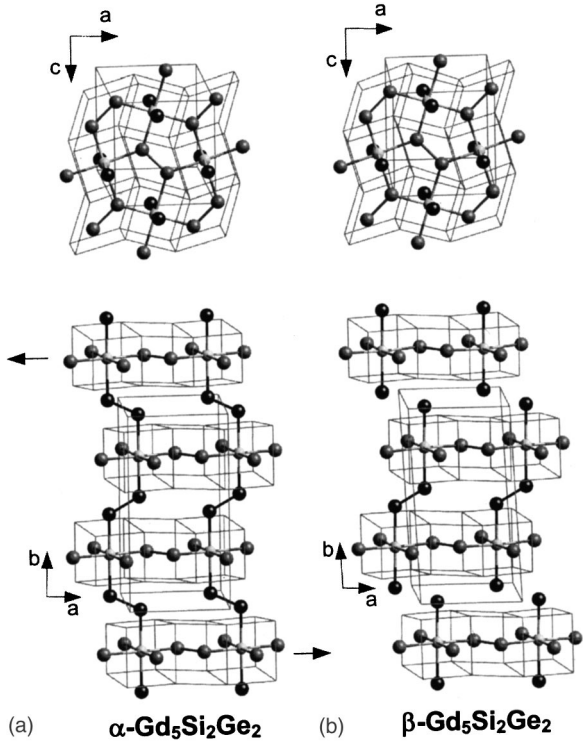
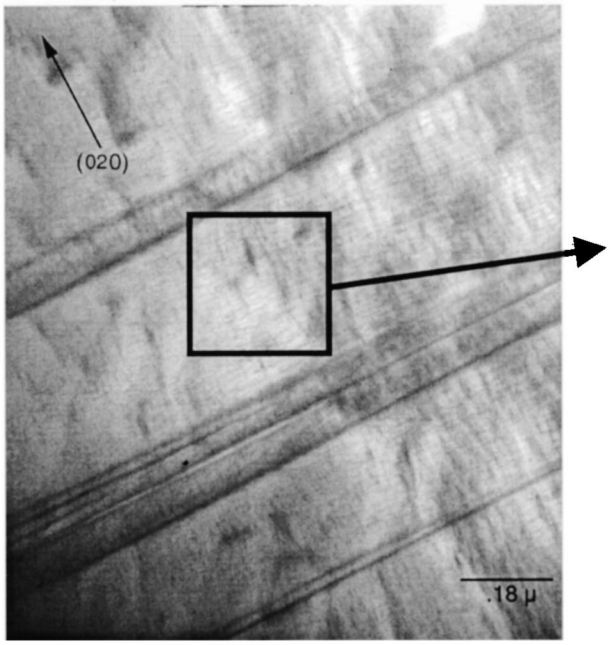
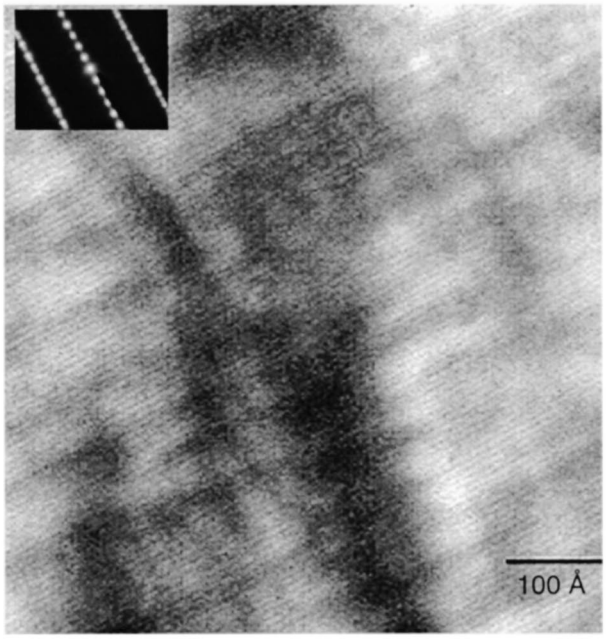


FIG. 1. The crystal structures of (a) α-$Gd_5Si_2Ge_2$ and (b) β-$Gd_5Si_2Ge_2$ shown along the (010) axis (top) and (001) axis (bottom). This figure is taken from Ref. 6. The (001) axis projection emphasizes a shear movement of the $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs, as well as breaking and forming (Si,Ge)-(Si,Ge) dimers (black circles). Gd atoms are light gray; (Si,Ge) atoms inside the $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs are dark gray. Each slab consists of two 3^2434 nets of Gd atoms with additional Gd atoms in the cubic voids and (Si,Ge) atoms in the trigonal prismatic voids.



(a)



(b)

FIG. 2. Microstructure of β-$Gd_5Si_2Ge_2$ at (a) low and (b) high resolution. The SAD pattern in (b) indicates that the diffuse lamellae streaks are parallel to the (020) plane.

secondary phases, unlike previous studies where various second phases and a linear feature were observed.[13,14] The microstructure of the material is shown in Fig. 2. Two features can be seen; what appears to be a sharply faulted structure is immediately obvious while a much finer diffuse lamellar structure can be observed across the entire region of Fig. 2(a) SAD patterns were obtained from areas containing only the

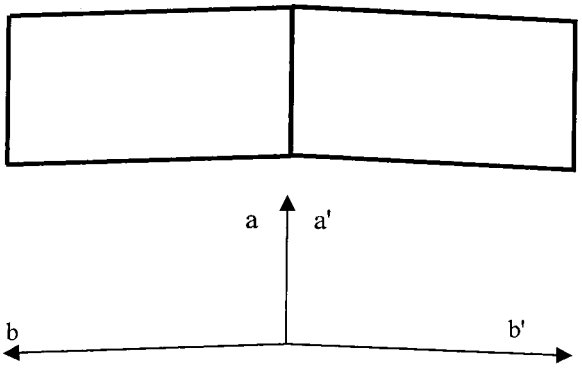


FIG. 3. Scheme for the twin law found in β-$Gd_5Si_2Ge_2$. The twin axis is the [100] crystallographic axis with $\mathbf{b}'=\mathbf{b}+\mathbf{a}(2b\cos\gamma)/a$ where $(2b\cos\gamma)/a=-0.2229$, $a=7.5891(17)$ Å, $b=14.827$ Å, $c=7.7862$ Å, and $\gamma=93.262(4)°$. Cell parameters are from Ref. 6.

lamellae, the apparent faults plus lamellae, and overlapping a fault boundary. No differences were observed between these respective SAD's, in all cases the patterns matched well with predicted patterns of β-$Gd_5Si_2Ge_2$, supporting the conclusion that structures observed here are not due to the formation of any secondary phases. High-resolution imaging of the structure, Fig. 2(b), shows that both the sharp faultlike structure and the diffuse lamellae streaks are parallel to the (020) planes.

SAD patterns obtained from the sample confirm the twin patterns in β-$Gd_5Si_2Ge_2$, as suggested in the single-crystal structure study.[6] The twin observed in β-$Gd_5Si_2Ge_2$ is a rotational twin with respect to the [100] axis (see Fig. 3). The twin law, which transforms one twin component to the other, can be seen as follows:

$$\mathbf{a}'=\mathbf{a},$$

$$\mathbf{b}'=\mathbf{b}+\mathbf{a}\left(\frac{2\mathbf{b}}{\mathbf{a}}\right)\cos\gamma\cong\mathbf{b}-0.2229\mathbf{a}\cong\mathbf{b}-\frac{2}{9}\mathbf{a},$$

$$\mathbf{c}'=-\mathbf{c},$$

$$\begin{pmatrix}\mathbf{a}'\\ \mathbf{b}'\\ \mathbf{c}'\end{pmatrix}=\begin{pmatrix}1 & 0 & 0\\ -\frac{2}{9} & 1 & 0\\ 0 & 0 & -1\end{pmatrix}\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix}.$$

Because of this twin relationship, $\mathbf{b}'=\mathbf{b}-(\frac{2}{9})\mathbf{a}$, $k'=k-(\frac{2}{9})h$, and reflections from the two twin domains coincide almost exactly when $|h|=0$ or 9. When $|h|=4$ or 5, the reflections from the two individuals are so close that, in most cases, they significantly overlap one another. In Fig. 4(a), the (200) reflection has a satellite at $(2, -\frac{4}{9}, 0)$, due to nonmerohedral twinning governed by the twin law above. The angle between the two twin cells is 5.7°, which compares well with the value calculated from the single-crystal data, i.e., $[2(\gamma-90°)=2(93.262°-90°)\cong 6.5°]$.[6] Figure 4(b) shows two twin grids, which can be compared with the SAD pattern shown in Fig. 4(a). Although these two twin components are related by C_2 rotation with respect to the crystallographic **a** axis, as shown in Fig. 4(b), the intensities of reflections from

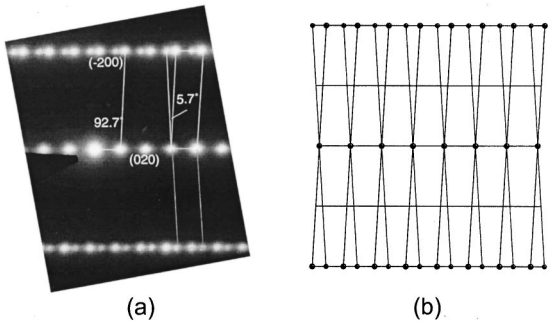


FIG. 4. (a) SAD pattern for β-$Gd_5Si_2Ge_2$ and (b) its corresponding twin grids.

the two components are not equivalent because the twin operator is not a symmetry operator of β-$Gd_5Si_2Ge_2$.

The shear movement of the $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs along the [100] axis is responsible not only for the $\alpha \rightarrow \beta$ phase transition, but also plays a crucial role for twin formation in β-$Gd_5Si_2Ge_2$. Figure 5 illustrates a model for the formation of twin boundaries during the phase transition. If twinning is absent in the β phase, alternate layers of (Si,Ge)-(Si,Ge) dimers that bond two $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs together in the orthorhombic α phase along the [010] axis are broken as two adjacent slabs shift in opposite directions along the crystallographic [100] axis [see Fig. 5(a)]. Twinning can be generated when two adjacent layers of (Si,Ge) dimers are broken at the same time. In this case, a single $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slab shifts with respect to its neighboring slabs [see Fig. 5(b)] and two different orientations of monoclinic cells are identified, which are related to each other by C_2 rotation along the [100] axis as mentioned previously. Consequently, nonmerohedral twinning occurs. One interesting feature of this model is that one false, irregular movement along the [100] axis can generate a twin. How often such irregular movement occurs determines whether the twin in β-$Gd_5Si_2Ge_2$ is a macroscopic or a microscopic one. All attempts to isolate one of the two twin domains in the SAD pattern failed, suggesting that the nonmerohedral twin found in β-$Gd_5Si_2Ge_2$ is more likely a microscopic one (i.e., the twin domain is smaller than the area selected by aperture). We also find that twinning in β-$Gd_5Si_2Ge_2$ is intrinsic because we could not find any area in β-$Gd_5Si_2Ge_2$ that was not twinned. It is possible that the apparent faults observed in the microstructure indicate some type of macroscopic twin. Since the movement needed to produce such a macroscopic twin as opposed to a microscopic one is identical, no apparent change in the SAD pattern would be observed. However, at this point this is simply speculation.

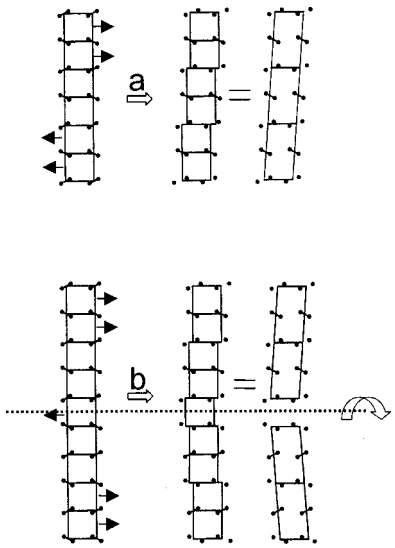


FIG. 5. A possible model for the formation of twins during the $\alpha \rightarrow \beta$ phase transition caused by shear movement along the crystallographic [100] direction. The arrows indicate the movement of $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs, thereby breaking the dimers which connect adjacent $^{\infty}_{2}[Gd_5(Si_2Ge_2)]$ slabs. No twinning requires the shift movement to involve pairs of slabs (a), while twinning occurs when there is an occasional shear movement of just a single slab, thereby creating twinned monoclinic cells (b). The dotted line indicates the C_2 twin axis.

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