Sandwichlike strain glass phase diagram of Ti_{49}Ni_{51-x}Pd_x

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Two kinds of phase diagrams can be observed in doped ferroic materials. A glass phase diagram is formed by
doping a nontransforming end into a ferroic matrix, while doping a transforming end forms phase diagrams with
a phase boundary separating two different ferroic phases. Here we report a phase diagram in which a strain glass
state is sandwiched between two distinct ferroelastic phases. This type of phase diagram in doped ferroelastic
materials bridges the one with a glass state and the one with a phase boundary. We thus establish a 3D phase
diagram of Ti_{50−y}Ni_{50+y}−xPd_x ternary alloys, in which the evolution of these different kinds of phase diagrams
can be observed. An understanding from the Landau free energy landscape suggests that the transforming doping
end plays three roles in influencing the ferroic matrix: (1) to destabilize the ferroic matrix phase, (2) to stabilize
another ferroic phase different from the matrix one, and (3) to create random local fields. The competition
between these effects determines various phase diagrams in doped ferroic materials. Thus our work may provide
an experimental foundation for a unified mechanism to all three kinds of phase diagrams.

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I. INTRODUCTION

Doping with defects is a common approach to improve
various physical properties of materials [1]. The well-known
examples include acceptor/donor-doped Si, which forms the
P-N junction, serving as the base of modern electronic industry
[2]. Doping also plays a crucial role in ferroic materials, an
important subgroup of smart materials which respond
hysteretically to electric, mechanical, or magnetic fields [3].
For example, doping results in various interesting phenomena
in ferroic materials, ranging from the glassy transition [4–11]
to the morphotropic phase boundary [12–17] to the aging effect
[18]. Those phenomena can either improve the functional
properties significantly or give rise to new physics.

The quenched-in disorders or defects give rise to the
frustration in a ferroic property (usually the ferroic order
parameter) such as strain, polarization, or magnetization, and
thus result in a glassy state in ferroic materials [19–21]. The
glassy state possesses a frozen and frustrated local ordering
of the ferroic order parameters rather than a long-range ferroic
ordering [19–21]. It is manifest in its nonergodic response and
slow dynamics [7,22]. Experimentally, the glassy phase is ob-
tained by doping a nontransforming end (without spontaneous
symmetry-breaking transformation) into a ferroic matrix (with
spontaneous symmetry-breaking transformation) [4–11]. The
nontransforming end can be considered as point defects
which create random local fields to hinder the long-range
ordering of ferroic order parameters [23–26]. With increasing
concentration of the nontransforming end, the long-range
ferroic ordering of the transforming matrix gradually loses
its thermodynamic stability. After the concentration exceeds a
critical value, the long-range ordering breaks whereas the
short-range ordering persists. In the past decades, such
a glassy state has been found in three primary ferroic systems
(i.e., ferromagnetics, ferroelectrics, and ferroelastics), and
elements include strain glass in Ti_{50}(Ni_{50−}D_x) (D=Fe, Co,
Cr, Mn) ferroelastic alloys [27,28], relaxors in La-doped
PZT ferroelectric ceramics [29,30], and cluster spin glass in
Au-Fe binary alloys [31]. Those reported glass-state-involved
phase diagrams in three ferroic systems possess a similar
configuration; i.e., there is a phase boundary separating a
ferroic long-range phase and a glassy state.

Differently from the above glass phase diagram, the phase
diagram constructed by two transforming ends (both with
spontaneous symmetry-breaking transformation) generally
possesses a phase boundary separating two different long-
range-ordered ferroic phases [12–15]. The most well-known
example is the phase diagram of lead zirconium titanate (PZT)
in which a phase boundary separating tetragonal and rhombo-
dedral ferroelectric phases allows giant piezoelectric responses
[12,13]. This phase boundary was termed the morphotropic
phase boundary (MPB), where the competition between the
two long-range ferroic orderings makes the variation of order
parameters fairly easy [12,15]. Recently, such an MPB phase
diagram was also discovered in ferromagnetics where giant
magnetostriiction was obtained [16,17]. Moreover, similar
phase diagrams with a phase boundary separating two different
ferroelastic phases exist in Ti_{50}Ni_{50−x}Ti_{50}M_{50} (M=Pt, Au, Pd)
shape memory alloys/ferroelastic systems as well [32–37].
All of the MPB phase diagrams are characterized by a phase
boundary separating two different long-range-ordered ferroic
phases.

Glass and MPB phase diagrams have been widely studied
for decades, but in a separate manner. The linking between
these two types of doping-induced phase diagrams is seldom
concerned. It seems that the nontransforming doping end
results in a glass phase diagram, while doping with the
transforming end leads to an MPB phase diagram. In the
present study, we showed that doping with the transforming

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FIG. 1. (a) The martensitic transformation start temperature ($M_s$) and entropy change ($\Delta S$) during martensitic and reverse martensitic phase transformations in Ti$_{49}$Ni$_{51-x}$Pd$_{x}$ alloys as a function of Pd concentration. (b1)–(b6) DSC curves of several typical compositions: (b1) 0Pd, (b2) 3Pd, (b3) 7.5Pd, (b4) 15Pd, (b5) 20Pd, and (b6) 25Pd.

end can give rise to a glassy state instead of MPB. Furthermore, a sandwichlike strain glass phase diagram in Ti$_{49}$Ni$_{51-x}$Pd$_{x}$ was established, where two different ferroelastic phases exist at two sides respectively and a strain glass state is sandwiched in between. In orientational glasses, phase diagrams with a similar shape where two long-range orientational orders are separated by a glassy state have been reported [38,39]. But how this kind of phase diagram relates with glass and MPB phase diagrams is still unclear. We then established a three-dimensional phase diagram, which bridges the glass and MPB, and it may be helpful to develop a unified understanding on all the doping-induced phase diagrams in ferroic materials.

II. EXPERIMENTAL PROCEDURE

Samples of Ti$_{49}$Ni$_{51-x}$Pd$_{x}$ alloys ($x = 0 \sim 25$, abbreviated by xPd hereafter) were prepared from highly pure metals (>99.95 at.%) by arc-melting under an argon atmosphere. The specimens were solution-treated at 1273 K for 24 h in evacuated quartz tubes, followed by water quenching. After hot rolling, the specimens were solution-treated at 1273 K for 1 h and subsequently quenched into water again. Latent heat of transformation was measured with a differential scanning calorimeter (DSC-Q200 from TA Company) with a cooling/heating rate of 10 K/min. Electrical resistivity (ER) of specimens was measured through a four-probe method with a constant current of 100 mA and a cooling/heating rate of 2K/min. In situ x-ray diffraction (Shimadzu 7000 XRD) measurement from high temperature to low temperature was used to identify the possible structural change. The possible strain glass transition was detected by dynamic mechanical analysis (DMA-Q800 from TA Instruments) using a step cooling method with a single cantilever mode in the frequency range from 0.2 to 20 Hz.

III. RESULTS

The composition dependence of entropy change ($\Delta S$) in both cooling and heating processes [Fig. 1(a)] exhibits an unexpected U curve, which is calculated by $\Delta S = \Delta H/M_s$, where $\Delta H$ is latent heat during martensitic or reverse martensitic transformation [i.e., the area under the endothermic/exothermic peaks in DSC curves as shown in Figs. 1(b1)–1(b6)]. $M_s$ is the martensitic transformation start temperature and $A_s$ is the reverse martensitic transformation start temperature. The martensitic transformation is generally considered as a first-order transformation, and its order parameter (spontaneous strain) will show a sudden jump at the transformation temperature during cooling and heating, and thus the latent heat of transformation will appear. Interestingly, as Pd content slightly increases from 0Pd to 7.5Pd, the entropy change drastically decreases to zero. Such a situation suggests that Pd atoms lower the thermodynamic stability of martensite and eventually result in a zero entropy change (i.e., nontransforming) region, being similar to the result in Ti$_{50}$Ni$_{50-x}$Pd$_{x}$ alloys with strain glass state [7,40]. However, it is worth mentioning that Pd atoms in Ti$_{50}$Ni$_{50-x}$Pd$_{x}$ alloys do not lead to a nontransforming region but result in a phase boundary separating B19' ($P_{21}/m$, monoclinic structure [33]) and B19 ($Pmnb$, orthorhombic structure [33]) ferroelastic phases [32–34]. The reason will be discussed later. Notably, the entropy change dramatically reappears when Pd content exceeds 15Pd, indicating the martensitic phase becomes stable again over 15Pd. This intriguing result is rarely reported in the prior reported strain glass cases [26,27,40].

It is notable that the original ferroelastic phase and the revived ferroelastic phase belong to two different structures, as supported by electrical resistivity and XRD measurements in Fig. 2. In Figs. 2(a1) and 2(a2), a sharp resistivity change at $M_s$ with an obvious hysteresis is observed at 0Pd and 3Pd during
FIG. 2. (a1)–(a6) Electrical resistivity curves of (a1) 0Pd, (a2) 3Pd, (a3) 7.5Pd, (a4) 15Pd, (a5) 20Pd, and (a6) 25Pd. All the ER results are normalized by the electrical resistivity at 300 K. (b1)–(b6) X-ray diffraction patterns of typical (110) peaks in B2 structure of (b1) 0Pd, (b2) 3Pd, (b3) 7.5Pd, (b4) 15Pd, (b5) 20Pd, and (b6) 25Pd at temperature far below $M_s$, as indicated by red circles and arrows in the corresponding resistivity curves.
FIG. 3. Anelastic property evolutions with temperature for different Pd concentrations, (a) 0Pd, (b) 3Pd, (c) 7.5Pd, (d) 15Pd, (e) 20Pd, and (f) 25Pd. The inset figures exhibit V-F law fitting of each strain glass transition. The ideal freezing temperature ($T_0$) yielded to be 204 K for 3Pd (b), 176 K for 7.5Pd (c), 209 K for 15Pd (d), and 220 K for 20Pd (e).

This $M_s$ change tendency suggests Pd doping lowers the thermodynamic stability of B19$'$ martensite while it stabilizes the B19 martensite. However, in the MPB phase diagram of Ti$_{50}$Ni$_{50}$Pd$_x$ ($x = 0 \sim 25$), Pd itself is unable to disturb the formation of the long-range-ordered B19$'$ ferroelastic phase. As the result, there is a phase boundary separating B19$'$ and B19 martensites. On the contrary, a slight deviation with 1 at. % Ni modification at ends, i.e., from Ti$_{50}$Ni$_{50}$/Ti$_{50}$Pd$_{50}$ to Ti$_{49}$Ni$_{51}$/Ti$_{49}$Pd$_{51}$, causes significant change: the phase boundary disappears, and instead, a strain glass region emerges, sandwiched between B19$'$ and B19 martensites. It is known that the excess of Ni reduces the stability of B19$'$ martensite as $M_s$ decreases from Ti$_{50}$Ni$_{50}$ to Ti$_{49}$Ni$_{51}$ [40,41]. Thus, under assistance of 1 at. % excess Ni, Pd is able to drive the system to a glassy state.

IV. DISCUSSION

We then try to figure out the underlying mechanism on how this 3D phase diagram forms by providing a qualitative explanation. Previous work on standard strain glass phase diagrams reveals that the nontransforming end contributes two parts of effects: a global effect, which decreases the thermodynamic stability of long-range-ordered martensite, and a local effect to generate random local energy barriers which frustrate the system and lead to a glassy state [27]. On the other hand, the MPB phase diagram is always attributed to the competition between two ferroic phases from each side. But the local effect due to transforming doping is always beyond consideration [12,15]. It seems that previous understanding on both glass phase diagrams and MPB phase diagrams is too confined to explain this 3D phase diagram, especially the sandwichlike glass phase diagram part.

In fact, introducing a transforming end may generate three different effects: (1) one global effect to destabilize the ferroic matrix phase, (2) another global effect to stabilize another ferroic phase different from the matrix one, and (3) a local effect to create random local fields. In the following, a
phenomenological Landau-type model is proposed to understand the 3D phase diagram in Fig. 4.

In the case of MPB, two different ferroic orderings compete with each other. A generic Landau polynomial of the two ferroic phases that captures the essential features of the martensitic transitions of the two martensites can be expressed as [42,43]

\[ F_A(x, T, \eta) = A_1\left(T - T_{cA}^0\right)\eta^2 + A_2\eta^4 + A_3\eta^6, \]

\[ F_B(x, T, \theta) = B_1\left(T - T_{cB}^0\right)\theta^2 + B_2\theta^4 + B_3\theta^6, \]

where \( x \) is the concentration of doping end, \( T \) represents temperature, and \( \eta \) and \( \theta \) are order parameters characteristic of the two martensitic phases. It should be noted that this is a simplified treatment. A more quantitative treatment requires the identification of the specific order parameters by symmetry analysis, and thus can be done with a more rigorous Landau polynomial based on those order parameters related to symmetries [44–47]. \( A_1 \sim A_2 \) and \( B_1 \sim B_3 \) are the expansion coefficients, related to the moduli of the system. Here they are treated as constants [42]. The effective transformation temperatures \( T_{cA}^0 \) and \( T_{cB}^0 \) are assumed to be linearly dependent on composition, \( T_{cA}^0 = T_{cA}^0 - \alpha x \) and \( T_{cB}^0 = T_{cB}^0 - \beta(1 - x) \). Such a linear dependence is consistent with the tendency of the transformation temperature as a function of composition in Fig. 4. The \( \alpha \) and \( \beta \) characterize the global effect strengths for different ferroic phases respectively [43]. The total free energy of the system is then written as [42]

\[ F(x, T, \eta, \theta) = A_1\left(T - T_{cA}^0 - \alpha x\right)\eta^2 + A_2\eta^4 + A_3\eta^6 + B_1\left(T - T_{cB}^0 - \beta(1 - x)\right)\theta^2 + B_2\theta^4 + B_3\theta^6 + C\eta^2\theta^2, \]

where \( C \eta^2\theta^2 \) describes the coupling between two order parameters. In the MPB phase diagram, the relative stability of these two ferroic phases varies with composition. At MPB, the free energies of the two phases are identical, that is, \( F_A = F_B \). A Landau free energy landscape of the system at MPB is then schematically shown in Fig. 5(a).

In order to better understand the MPB phase diagram, we provide the free energy landscapes along different order parameter directions by Eq. (3) with suitable coefficients in Figs. 5(b1)–5(b3), which schematically shows the evolution of Landau free energy landscapes with composition at a certain temperature (below \( M_c \)) in the Ti50Ni50–Pd system. At the doping-free (Ti50Ni50, one end of the MPB phase diagram) case [Fig. 5(b1)], B19’ martensite is the only thermodynamic stable state below \( M_c \) (illustrated by two-energy valleys in the blue curve), while B19 martensite is unstable (illustrated by single-energy valley in the green curve). With doping Pd (i.e., increasing Ti50Pd50 concentration, the other end of the MPB phase diagram), the free energy of B19 martensite gradually declines, while the free energy of B19’ martensite starts to increase. The free energy of B19 martensite becomes comparable with that of B19’ martensite near the phase boundary, as shown in Fig. 5(b2). When Pd concentration further increases to the Ti50Pd50-rich side, the free energy of B19 martensite begins to be lower than that of B19’ martensite. Thus, B19 martensite, instead of B19’ martensite, turns thermodynamically stable, and becomes the only thermodynamic stable phase at the other end composition (Ti50Pd50) at last [see Fig. 5(b3)].

Doping Pd may also generate local energy barriers [denoted by zigzag lines near the ordinate origin in Fig. 5(b2)]. However, these local energy barriers are too small to hinder the formation of long-range-ordered martensites. Thus, previous models on MPB generally omitted the local effect, and only considered the competition between the two global effects.

In the case of the glass phase diagram, the nontransforming dopants decrease the global transition temperature while they create random local fields. The former is described by the composition \( x \) dependence of transition temperature (\( T_c \)), i.e., \( T_c = T_c^0 - \alpha x \). The latter is considered as a spatially distributed random field \( \sigma(\vec{r}) \) coupled to the order parameter. The free energy at location \( \vec{r} \) is given by [43]

\[ f_A(x, T, \eta(\vec{r})) = A_1\left[T - (T_c^0 - \alpha x)\right]\eta^2 + A_2\eta^4 + A_3\eta^6 \]

\[ + A_4\eta^4 - \alpha(\vec{r})\eta^4 \]

Thus the free energy of the whole system is

\[ F_A(x, T, \eta) = \int d\vec{r}[f_A(x, T, \eta(\vec{r}))]. \]

Such a model is suitable to describe the reported glass phase diagrams of Ti50Ni50–D1, and Ti50Pd50–D5 systems with the ferroic orderings of B19’ and B19, respectively [27,48]. D represents the nontransforming dopants, such as Mn, Cr, Fe,
V, etc., which create strong random local fields to the systems and give rise to the glassy state.

In the case of the sandwichlike phase diagram, all of the above three effects should be considered, but none of them is dominant. Consequently, all the effects contribute to the free energy, which is given by

\[ F(x, T, \eta, \theta) = \int dr \left[ f_A(x, T, \eta, \theta) + f_B(x, T, \eta, \theta) + C_\eta \phi_\eta \phi_\eta^* \right] \quad \text{(6)} \]

In order to schematically draw the Landau free energy landscapes along two order parameter directions according to Eq. (6), we first consider the system as a homogeneous model like Eq. (3), and then add the local effect as random noise in the energy landscape, as used in the spin glass literature [4]. Thus, the local effect is denoted by zigzag lines near the ordinate origin in Fig. 5. Compared with Ti50Ni50, Ti49Pd51, the starting point of the sandwichlike glass phase diagram of Ti49Ni51−x−y, Pdx, has already possessed low intensity of local energy barriers caused by extra Ni atoms. Thus, local random fields in Ti49Ni51−x−y, Pdx become stronger than those in Ti50Ni50−x−y, Pdx at the same Pd concentration.

The sandwichlike strain glass phase diagram is then explained by Figs. 5(c1)–5(c3) which are obtained according to Eq. (6) with artificial coefficients. As shown in Fig. 5(c1), though the matrix becomes “dirty” compared with Ti49Ni50, this part of the local energy barriers in the matrix is not strong enough to interrupt the formation of B19′ martensite [40,41]. When the other end member (Ti49Pd51) is introduced, B19′ martensite further loses its thermoelastic stability while the stability of B19 martensite starts to increase. However, the most notable point in Fig. 5(c2) is that doping Pd atoms (i.e., Ti49Pd51) also generates random local energy barriers. This part of local energy barriers caused by Pd itself is still not enough to drive the system into a glass state [see Fig. 5(b2)], but with the assistance of local energy barriers existing in the matrix (Ti49Ni51), the total local energy barriers finally beat the thermoelastic driving force for long-range-ordered martensites (including both B19′ and B19 martensites), and result in a glassy state. Further increasing Pd concentration to the Ti49Pd51-rich side, the free energy valley of B19 martensite becomes even deeper, and the local energy barriers to interrupt the formation of B19 martensite become smaller because Ti49Pd51 prefers B19 martensite, as shown in Fig. 5(b3).

The competition among the three effects explains why the 3D phase diagram of Ti50−x−y, Ni50−x−y, Pdx forms. In the MPB phase diagram of Ti50Ni50−x−y, Pdx, the two competing global effects are dominant, while the local effect is negligible. In the sandwichlike phase diagram of Ti49Ni51−x−y, Pdx, the net global effect (from the competition of two global effects) and the local effect are comparable with each other, and the competition between them results in the sandwiched glass region. Thus, the transforming doping end is considered to be able to create a local effect (i.e., random local energy barriers). This is supported by our sandwichlike phase diagram. Last but not least, one may easily imagine the phase diagram with further modifying two ends to Ti48Ni52/Ti48Pd52: it should be a traditional strain glass phase diagram since the Ti48Ni52 end is nontransforming (strain glass) [40], while the Ti48Pd52 end is transforming [49]. Thus, the sandwichlike strain glass phase diagram of Ti48Ni51−x−y, Pdx serves as a bridge linking the MPB phase diagram of Ti50Ni50−x−y, Pdx and the strain glass phase diagram of Ti48Ni52−x−y, Pdx.

V. CONCLUSIONS

In conclusion, we reported a sandwichlike strain glass phase diagram in Ti50Ni51−x−y, Pdx, and established a 3D phase diagram of Ti50−x−y, Ni50−x−y, Pdx. This sandwichlike glass phase diagram enables us to have a comprehensive understanding on how a transforming doping end influences a transforming matrix: (1) to destabilize the ferroic matrix phase, (2) to stabilize another ferroic phase different from the matrix one, and (3) to create random local fields. This understanding may guide us to unify prior models on respectively explaining the glass and MPB phase diagrams, and may bring about new physics on doping effects.

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