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Study of the phase transformations in Ni_2MnGa by capacitance dilatometry

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Abstract

High precision capacitance dilatometry has been used to study the phase transformations in a Ni_2MnGa single crystal. The results show that capacitance dilatometry is an effective method to study the phase transformations. The thermal strain accompanying the martensitic transformation was not reproducible, but became more reproducible with the application of external stress. The first-order character of the martensitic transformation was enhanced by external stress. The intermediate transformation temperature decreased with increasing external stress with a temperature coefficient of -2.40 K MPa^{-1}. The coefficient of thermal expansion was 1.7×10^{-5} K^{-1} for the parent phase and 1.4×10^{-5} K^{-1} for the intermediate phase.

1. Introduction

The Heusler alloy Ni_2MnGa is a ferromagnetic shape-memory alloy. At temperatures above the martensitic transformation, near-stoichiometric Ni_2MnGa alloys exhibit pronounced but incomplete, premonitory, phonon softening of the $[\zeta\zeta 0]$ TA_2 bulk phonon mode at $\zeta = 0.33$ [1]. It has been suggested that a premartensitic phase occurs as a result of the anharmonic coupling between this phonon mode and homogeneous deformations associated with the elastic constant $c' = (c_{11} - c_{12})/2$ [2]. The austenite (parent) phase has a cubic structure with lattice parameter, $a_{\text{cubic}} = 0.582$ nm. The premartensite phase (previously called the intermediate phase [1]) was recently characterized as having an orthorhombic unit cell with lattice parameters $a_{\text{ortho}} = \frac{1}{\sqrt{2}}a_{\text{cubic}}$, $b_{\text{ortho}} = \frac{3}{\sqrt{2}}a_{\text{cubic}}$ and $c_{\text{ortho}} = a_{\text{cubic}}$ [3]. At low temperature, five-layered martensite, a body-centred tetragonal structure with $a_{\text{tet}} = 0.590$ nm, $c_{\text{tet}} = 0.554$ nm, appears in near-stoichiometric Ni_2MnGa [4].

It has been acknowledged that the intermediate transformation is a weak, first-order transformation [5]. Therefore, only a few experimental techniques, such as dynamical mechanical analysis (DMA) [6], low-field AC susceptibility [5], and modulated DSC [5], have been used to study this transformation.

Capacitance dilatometry is a convenient technique with which to measure the coefficient of thermal expansion, α, and its variation with temperature [7]. Its main advantage is its high precision for the detection of sample length change. In a previous study by one of the present authors, a departure from cubic symmetry in the parent phase for a martensitic system at temperatures well above the traditional transformation temperature was observed by using this technique [8]. Thus, this could be a useful method to study the precursor effects in association with the martensitic transformation in Ni_2MnGa.

In the present paper, dilatometry studies are provided for a Ni_2MnGa single crystal. Both the martensitic and premartensitic transformations are evident. The effect of external stress on the intermediate phase transformation was also investigated.

2. Experimental details

A Ni_2MnGa single crystal was spark machined to produce a right prism of material, having {100} faces. The respective opposite faces were lapped to be flat and parallel to within a few minutes of arc. The final dimensions of the approximate cube of single crystal were $2.82 \times 3.45 \times 3.38$ mm^3, so that throughout the experiments a knowledge of the distinct $\langle 100 \rangle$ directions in the crystal could be maintained. For the convenience of data presentation the three $\langle 100 \rangle$ directions were labelled the *A*, *B* and *C* directions, corresponding to the 2.82, 3.45 and 3.38 mm sides, respectively.

The expansion measurements were conducted in a three-terminal capacitance dilatometer identical in design to that of White and Collins [7], in which the capacitance cell, machined from oxygen-free, high conductivity (OFHC) copper, is approximately 50 mm long. Ideally, a capacitance gap of about 0.3 mm exists between the upper OFHC copper plate and the top surface of the sample, if the sample is a conductor and can be machined to fill the cell, or an OHFC copper plate on top of the sample if it is not. As has been illustrated in an earlier publication reporting In–Tl single-crystal measurements [9], for a sample which is shorter than ideal, it is held between the latter, copper plate and an OFHC copper spacer, by light springs. The spacer is machined so that the capacitance gap is still approximately 0.3 mm. A gap of this size leads to a capacitance of around 4.5 pF, which, using an Andeen–Hägerling 2500A bridge, can be measured to a precision of about 1 part in 10^6.

The presence of the light springs clamping the crystal between the capacitor electrode and the spacer means that a very weak compressive force along the measurement direction is always applied to the sample. By using springs with different strengths, compressive stresses of different levels were applied to the sample along the measurement direction. The spring constants were determined for each of the springs in use by independently measuring extensions under small applied loads. In order to produce a tensile stress along the measurement direction, a uniaxial clamp was used to compress the crystal in a direction perpendicular to the measurement direction. Data collections over specific temperature ranges using a particular orientation of the crystal and stress configuration were repeated a few times to examine the reproducibility of the test result.

An optical microscope equipped with a temperature-controlled stage, which can directly observe the surface relief during martensitic transformation, was used as a complementary method to the dilatometry studies. Unfortunately, the temperature sensor of the temperature-controlled stage does not contact with the sample directly, which results in a difference between the temperature of the sample and the temperature recorded in the micrograph. Normally, the sample temperature was higher than the recorded temperature. This made it impractical to compare directly the temperatures from the dilatometry and those recorded on the optical micrographs.

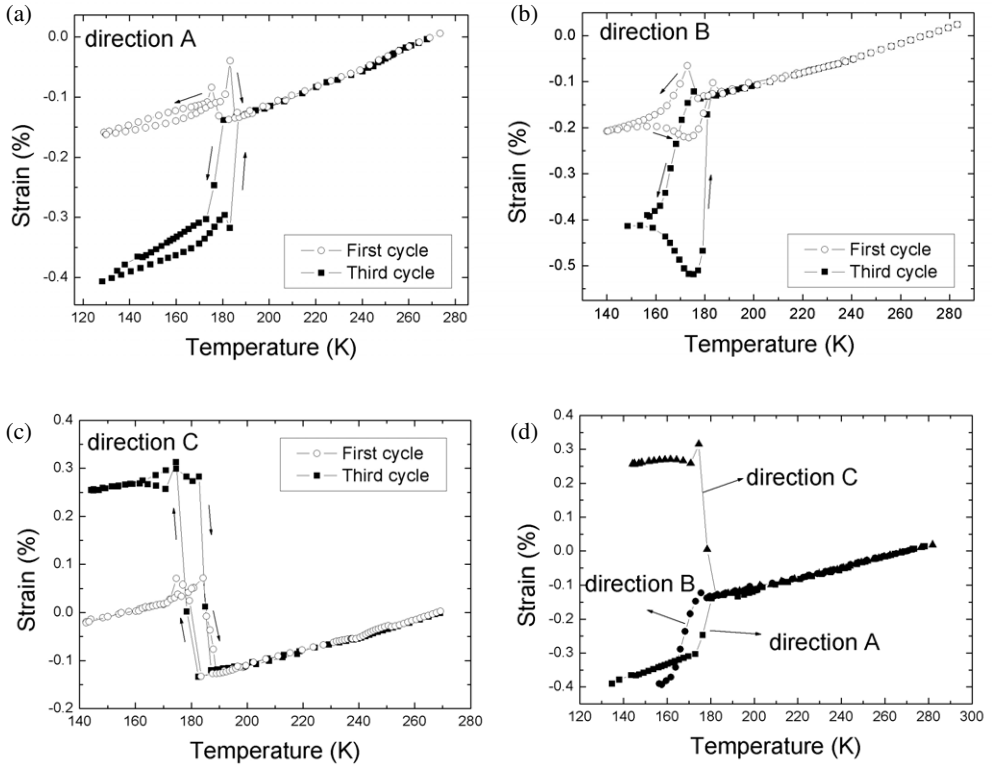

Figure 1. The change of strain with temperature for a Ni_2MnGa single crystal having {100} faces and measured along each of the three ⟨100⟩ directions, under very weak stress, intrinsic to the dilatometer, as explained in the text. The ⟨100⟩ directions were identified from the exact dimensions of the crystal and the measurements are for (a) along the 2.82 mm length, direction *A*, (b) along the 3.45 mm length, direction *B*, (c) along the 3.38 mm length, direction *C*, and (d) the comparison of the results among the three different directions, *A*, *B* and *C*, for the initial cooling cycle in each case.

3. Results

Results from measurements with the crystal along the three different ⟨100⟩ directions under very weak compressive stress, approximately 0.1 MPa, are presented in figure 1. The martensitic transformation is obvious from the large discontinuity in thermal strain. At temperatures above the martensitic transformation, the thermal strain versus temperature curves are reproducible, and show no difference along the different directions. But the results around the martensitic transformation temperature are non-reproducible though the measurements of thermal strain were under exactly the same conditions. With the onset of the martensitic transformation, it was observed that along directions *A* and *B* the sample sometimes shrank, but sometimes expanded. Along direction *C*, the sample always expanded. The magnitudes of the transformation strains for different thermal cycles were also different. It was reported that the bulk thermal strains accompanying the martensitic transformation in Ni_2MnGa are unpredictable without an external mechanical stress or an applied magnetic field [10]. However, in the present case, this appeared to be only part of the reason for the non-reproducibility of the experimental results, as will be discussed later.

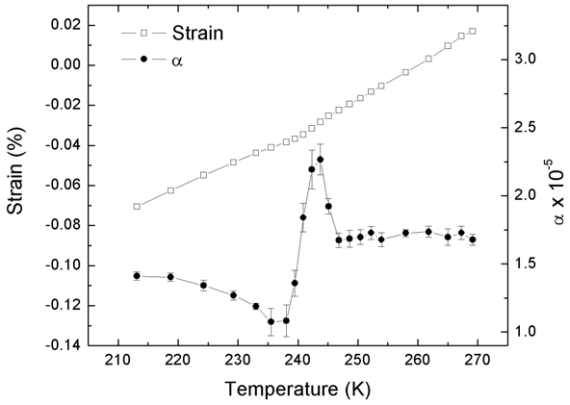

Figure 2. The temperature dependences of strain and α around the intermediate phase transformation for Ni_2MnGa single crystal, measured along a [100] (direction *B* from figure 1) under very weak stress along the direction of the strain measurement.

Around the intermediate phase transformation temperature, T_I (237 K), which was determined earlier for a piece of this crystal by an x-ray diffraction experiment measuring the change of the intensity of the (400) peak of the intermediate phase [11], only a very slight change in the slope of the strain versus temperature curve (figure 2) could be observed. Since the intermediate transformation is a weak, first-order transformation, the change of the slope is not distinct. By numerically differentiating the strain versus temperature curve, the linear expansion coefficient, α, could be obtained and it is also presented in figure 2. Because there are only slight differences amongst the data for the three different directions, only the data along direction *B* are shown here. A change of α around the intermediate transition can be found in the α versus temperature curve, which clearly shows the existence of the intermediate transition in the sample. By linearly fitting the strain versus temperature curve, the value of α for the intermediate phase was determined to be 1.4×10^{-5} K^{-1}, while that for the parent phase was 1.7×10^{-5} K^{-1}.

When the sample was compressed with a moderate stress, about 1.5 MPa, applied along direction *A* by using stronger springs within the expansion cell, the strain versus temperature curves became reproducible, as shown in figure 3. The sample shrank with the onset of martensitic transformation due to the compressive external stress. In the vicinity of the intermediate transformation, an evident change of thermal strain was observed. The sample first shrank, then expanded with decreasing temperature.

When the sample was compressed perpendicular to the measurement direction with a much stronger stress, about 5 MPa, the sample showed an opposite behaviour around the intermediate transformation temperature in comparison with the sample under compressive stress. Upon cooling through the intermediate phase transformation, the sample first expanded, and then shrank, while at the martensitic transformation the crystal expanded (figure 4). A small hysteresis is found for the intermediate transformation, as shown in the inset in figure 4. This is also consistent with the intermediate transformation being a weak, first-order transformation [5]. Though a stronger stress was applied, the results from different thermal cycles were non-reproducible at temperatures around martensitic transformation.

The surface relief associated with the martensitic transformation in two consecutive thermal cycles was observed using a microscope with a temperature-controlled stage. The results are shown in figure 5. Obviously, the sequences of the formation of surface twins and

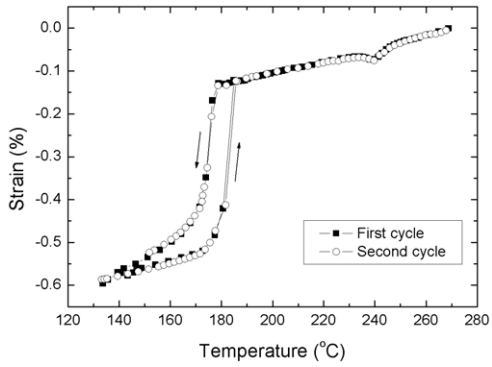

Figure 3. The strain versus temperature data along direction *A* with a stress of 1.5 MPa applied along the strain measurement direction.

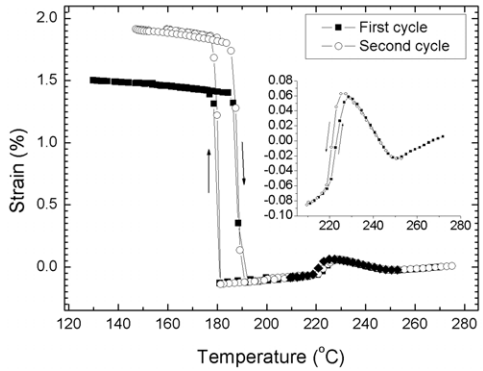

Figure 4. The strain versus temperature data along direction *A* with a stress of 5 MPa applied perpendicular to the strain measurement direction.

the final surface morphology were not the same between the two thermal cycles. This indicates that the formation of martensitic variants in Ni_2MnGa is unpredictable when there is no external constraint. But in addition, from the appearance of the surface of the crystal on being returned to room temperature, it is clear that its single-crystal quality is maintained following thermal cycling through the two structural transformations which occur upon cooling, at 237 and 180 K, respectively, as has been found previously in x-ray diffraction studies [11].

4. Discussion

4.1. The strain anomaly at the intermediate transformation

While the intermediate phase transformation has generally been described as 'weakly first order', the nature of the strain anomaly (figure 2) is not the discontinuity which one would normally expect for a truly first-order phase transition. However, the calorimetry data for a crystal exhibiting the intermediate phase transition (sample 2 of Mañosa and Planes [5]) also shows a very weak anomaly and not the discontinuity to be expected of a first-order transition. Thus there is clearly some doubt on the real definition of the thermodynamic order of the transition to the intermediate phase. In addition, the intermediate phase transition is

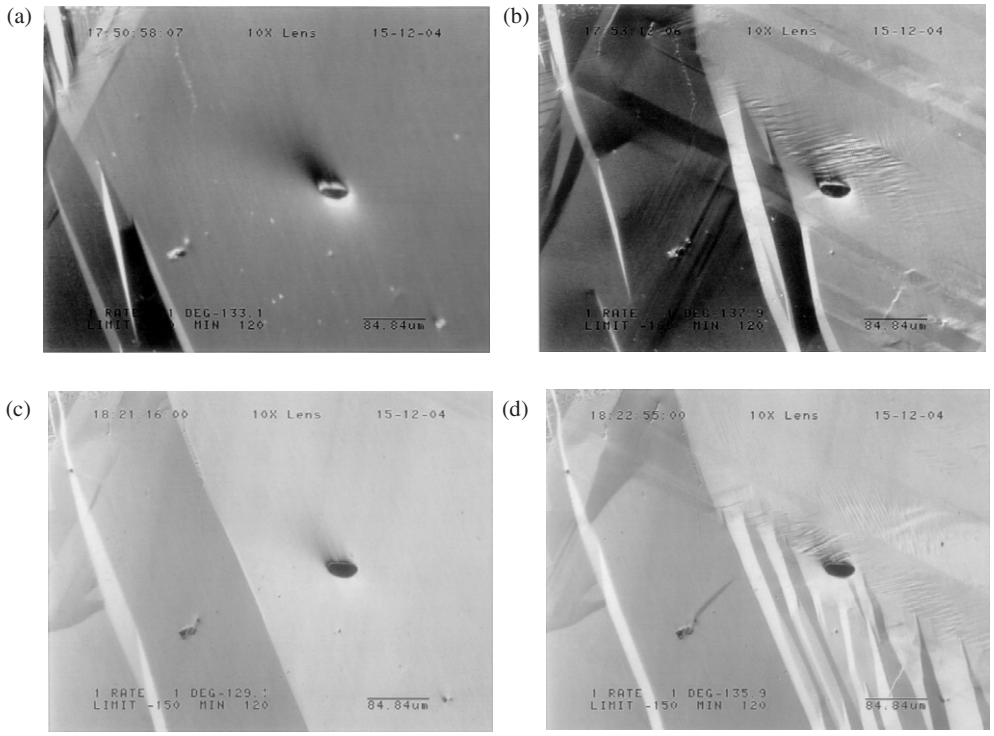

Figure 5. *In situ* observation of the surface relief during two consecutive thermal cycles: (a) martensitic transformation in progress during the first cycle; (b) after transformation during the first cycle; (c) transformation in progress during the second cycle and (d) after transformation during the second cycle.

accompanied by a small dip in the c_{44} elastic constant [12] in the vicinity of T_I, so that the measured anomaly in thermal strain could be a consequence of this anomaly in the elastic constant.

4.2. The influence of external stress on the thermal strain around the intermediate transformation

The influence of external stress on the intermediate transformation is summarized in figure 6. The area and height of the peaks which appeared in the thermal strain curves around the intermediate transformation, increased with the increase in the stress level. This agreed well with the theoretical prediction of the Mañosa *et al* [12] that the first-order character of the intermediate transformation could be enhanced by the application of external stress. The thermal strain, ε, under external stress, around the intermediate transformation consisted of three contributions, the phase transformation strain, ε_{tr}, the elastic strain, ε_{el}, and the thermal expansion strain, ε_{th}, i.e.

$$\varepsilon(T,\sigma) = \varepsilon_{tr}(T,\sigma) + \varepsilon_{el}(T,\sigma) + \varepsilon_{th}(T). \tag{1}$$

Here, T represents temperature and σ represents external stress. ε_{tr} is the strain accompanying the transformation from the parent phase to the intermediate phase, which is very small, according to the present experimental results. In the vicinity of transformation, over a temperature increment, ΔT, ε_{th} is given by $\alpha\Delta T$, where α is the coefficient of thermal

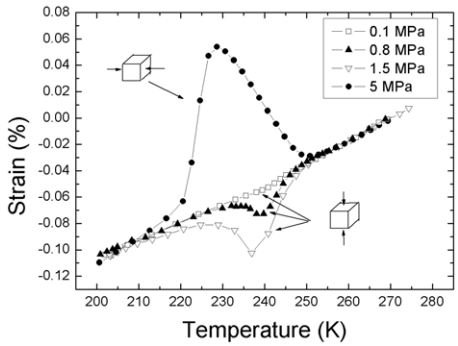

Figure 6. The strain versus temperature curves in the vicinity of the intermediate phase transformation, for different applied stresses.

expansion. ε_{el} can be expressed as $\varepsilon_{el} = \sigma/E(T,\sigma)$. Here E is the elastic modulus. Accompanying the phonon softening, the elastic modulus changes significantly around the intermediate transformation in Ni_2MnGa alloys. It first decreases and then increases with decreasing temperature [6, 13]. Hence, when the sample was under compressive stress, ε_{el} first decreased and then increased with decreasing temperature, and vice versa when the sample was under tensile stress. The change of ε_{el} can also be enhanced by increasing the stress level. Therefore, it was the contribution of ε_{el} that resulted in the stress-level-dependent behaviour of thermal strain around the intermediate transformation temperature.

4.3. The influence of the stress on the intermediate transformation temperature

It can also be seen from figure 6 that T_I decreases with the increasing compressive stress. According to the Clausius–Clapeyron relationship, the variation in the transformation temperature with the external stress is given by

$$\frac{dT}{d\sigma} = -\frac{T_0 \Delta\varepsilon}{\Delta H} \tag{2}$$

where T is the transformation temperature, σ is the stress, T_0 is the equilibrium transformation temperature, $\Delta\varepsilon$ is the strain accompanying the phase transformation and ΔH is the latent heat. For the transformation from the parent phase to the intermediate phase, $\Delta H < 0$ [5], $\Delta\varepsilon < 0$, therefore $dT/d\sigma < 0$, consistent with the experimental observations in figure 6.

Taking the minimum or maximum in the measured strain versus temperature (figure 6) to be a self-consistent definition for the parent to intermediate phase transformation temperature, a value for $dT/d\sigma = -2.40$ K MPa^{-1} has been determined from the present thermal strain data. By comparison with this coefficient, a value of -1.7 K MPa^{-1} can be derived from data for the stress dependence of T_I defined as the minimum in the relative change in elastic constant, $\Delta c_{44}/c_{44}$, versus temperature by Mañosa *et al* [12], where the stress was a compression applied along [001] and the crystal was cooling. However, when the crystal was being heated this same definition of T_I led to an increase in T_I with applied stress.

4.4. The influence of external stress on the coefficient of thermal expansion

From the strain versus temperature data in the vicinity of the intermediate phase transition (figure 6) it is clear that stress level has no obvious influence on the thermal expansion coefficient of the parent phase or that for the intermediate phase, once the temperature has

fallen sufficiently for the transformation to the intermediate phase to be complete, typically below 200 K. However, between this temperature and the temperature for the onset of the intermediate phase transformation, the thermal strain data were found to be highly anomalous and dependent on the applied stress direction in relation to the direction of the linear thermal strain measurement. This is to be expected for a uniaxial stress applied to a crystal undergoing a transformation to an orthorhombic structure.

4.5. The non-reproducibility of the experimental results around the martensitic transformation temperature

In the capacitance dilatometer, two parallel copper plates compose the capacitor. The sample is in contact with the lower copper plate. The change of the sample length causes a displacement of the lower copper plate relative to the upper one, and therefore a change of the capacitance. In order to resolve accurately the change of sample length from the change of the capacitance, many factors should be considered [14]. The tilt of the lower copper plate is one among them. A tilt of 10 min can result in an error of 0.015%. From figure 5 it can be seen that the surface relief accompanying the martensitic transformation can result in a very rough surface. This causes a change in the surface tilt of the lower copper plate. Unfortunately this change is not measurable. So the experimental results cannot be corrected and a strain anomaly is found in the result. A similar strain anomaly due to surface relief has been observed in a $Ni_{0.625}Al_{0.375}$ single crystal on the same dilatometer as well [15], although in the case of the transformation temperature range in $Ni_{0.625}Al_{0.375}$ the thermal strain along any one cube axis for a similarly machined {100} crystal was always reproducible for a fixed applied stress level.

Figure 5 also shows that the surface relief associated with the martensitic transformation varies from one thermal cycle to another. As a result, the strain versus temperature curves show non-reproducibility. It should be noticed that when the sample was under a moderate stress of 1.5 MPa along the measurement direction the thermal strain became reproducible (figure 3), whereas when the sample was under a strong external stress of 5 MPa perpendicular to the measurement direction the thermal strain continued to be non-reproducible (figure 4). In this latter case there remain different possible configurations for the martensite variants on the crystal surface, which is not so when a moderate stress is applied to the surface itself.

4.6. The advantages and disadvantages of capacitance dilatometry in studying the phase transformations in Ni_2MnGa

From the current experimental results, it can be concluded that capacitance dilatometry is an effective method to study the intermediate transformation in Ni_2MnGa. On account of the sensitivity of this technique to surface tilts, it is impossible to use it to obtain an accurate value of thermal strain accompanying the martensitic transformation unless an appropriate stress field can be applied to the crystal to remove the possibility for multi-variant formation along the measurement direction, as has been demonstrated previously for the cubic to tetragonal transformations in V_3Si [8] and In–Tl [16] or for the cubic to orthorhombic transformation in $Ni_{0.625}Al_{0.375}$ [17]. Nevertheless, the technique remains very sensitive to the onset of a martensitic transformation and, hence, the determination of transformation temperatures.

5. Conclusions

In the present paper, capacitance dilatometry has been used to study the phase transformations under different external stresses in a single-crystal Ni_2MnGa alloy. The thermal strain

accompanying the martensitic transformation was not reproducible, but could be made more so with the application of external stress. The results confirmed that the intermediate transformation is a weak, first-order phase transition. When the intermediate transformation occurs, the thermal strain first decreases, then increases with decreasing temperature under compressive stress applied along the direction measurement of thermal strain. The intermediate transformation temperature decreased with increasing applied stress and showed a stress coefficient of -2.40 K MPa^{-1}. In the vicinity of the transformation to the intermediate phase, the coefficient of thermal expansion was 1.7×10^{-5} K^{-1} for parent phase, and 1.4×10^{-5} K^{-1} for intermediate phase.

Acknowledgments

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