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Characteristics of the premartensitic transition strain in ferromagnetic shape memory $Ni_{50.5}Mn_{24.5}Ga_{25}$ single crystals

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Abstract
By measuring the strain across the premartensitic transition without and with external dc magnetic fields applied along the [001] and [010] directions of the parent phase, respectively, the characteristics of the premartensitic transition strain is investigated in detail. It was found that not only does the premartensitic transition temperature pronounce a more rapid decrease, but the premartensitic transition strain also exhibits a larger change for a field applied along the [010] direction than does a field along the [001] direction. In accord with a previous model, the present results confirm that the magnetoelastic interaction is responsible for the premartensitic transition, and the magnitude of the magnetoelastic interaction in the [010] direction is stronger than that in the [001] direction.

1. Introduction

Ni–Mn–Ga alloys with composition close to the stoichiometric Heusler Ni_2MnGa ($L2_1$ structure) have been attracting investigation due to their unique precursor phenomena at temperatures above the martensitic transformation. The precursors have been observed by many different experimental techniques such as x-ray [1, 2], neutron scattering [3–6], specific heat [7], magnetic susceptibility [8], magnetization [9] and ultrasonic measurements [10, 11]. It has been found that, depending on the specific composition [12, 13], at a given temperature (T_p) above the martensitic transformation temperature (T_M), the TA_2 soft phonon freezes and a micromodulated structure develops. This micromodulated structure occurring via a premartensitic (intermediate) phase transition has been studied by high-resolution transmission electron microscopy and has been shown to retain the cubic symmetry of the parent phase [12, 14]. The premartensitic (or intermediate) transition has been shown to be a weakly first-order transition, and to originate from the magnetoelastic coupling between the magnetization and the phonon, as suggested by a new Landou type model [15] and a mean-field and Monte Carlo simulation study [16]. However, it is generally believed that except for a strain observed in a uniaxial external stress [14] associated with the premartensitic transition, there is no other strain evidence corresponding to this structural transition. In this paper, we report the first direct strain characteristic of the premartensitic transition for a free $Ni_{50.5}Mn_{24.5}Ga_{25}$ single crystal sample grown by the Czochralski method. The premartensitic transition is characterized by a peak in the ε–T curve well above the martensitic transformation temperature T_M. Strain as a function of temperature measured under the different external magnetic fields shows clear evidence that the premartensitic transition temperature T_P and premartensitic transition strain (ε_P) are strongly dependent on the applied field. The field dependence of both T_P and ε_P demonstrates that the magnitude of the magnetoelastic interaction depends upon the direction of the applied magnetic field.

2. Experiment

The starting materials of the nonstoichiometric $Ni_{50.5}Mn_{24.5}Ga_{25}$ single crystal were prepared from metal elements Ni, Mn and Ga with purity of 99.95%. The single crystal was grown in the [001] direction according to the cubic parent phase by an MCGS-3 CZ (Czochralski) instrument with a cold crucible system. The grown rates of 12–15 mm h^{-1} and the rotation rate of 30 rpm were adopted. The single crystal was cut into $1 \times 6 \times 6$ mm pieces for strain measurements, and oriented by back-reflection Laue diffraction so that two perpendicular square sides of the sample are parallel to the [001] direction and [010] direction, respectively. The metal strain gauges with maximum measurement of 5% and the highly elastic epoxy resin were utilized to ensure measurement reliability and avoid gauge debonding. Magnetic field dependencies of magnetization were performed by a superconducting quantum interference device magnetometer (Quantum Design MPMS). Electrical resistivity was measured by a standard four-probe technique in a zero magnetic field. The magnetic susceptibility measurement was performed by a susceptometer with an ac magnetic field of 5 Oe and a frequency of 77 Hz over a wide temperature range. The temperature, alternating between cooling and heating, was varied at about 2 K min^{-1}.

3. Results and discussion

Figure 1 shows the temperature dependence of ac susceptibility χ measured in the cooling run, with the ac fields applied along the [001] direction of the free sample. One can easily see that the martensitic transformation start temperature T_M and the Curie temperature T_C marked in figure 1 are about 123 and 375 K, respectively. Moreover, as marked by an arrow between T_M and T_C, a relative dip-like anomaly at about 202 K is clearly observed, which corresponds to premartensitic transition temperature T_P in the cooling run. The inset in figure 1 is a plot of the resistance as a function of temperature upon cooling for a sample cut from the same piece. The temperature dependence can be described as approximately three linear regions except at the transitions. A large jump near 123 K corresponds well to the martensitic transformation observed by ac susceptibility. This is a natural consequence of a first-order structural transition. At a higher temperature T_P, near 202 K, a change in the slope of the resistance is clear. The T_P determined by the R–T measurement is nearly the same as the dip-like temperature observed in the χ–T curve. The close correspondence demonstrates unambiguously a premartensitic transition for the $Ni_{50.5}Mn_{24.5}Ga_{25}$ sample.

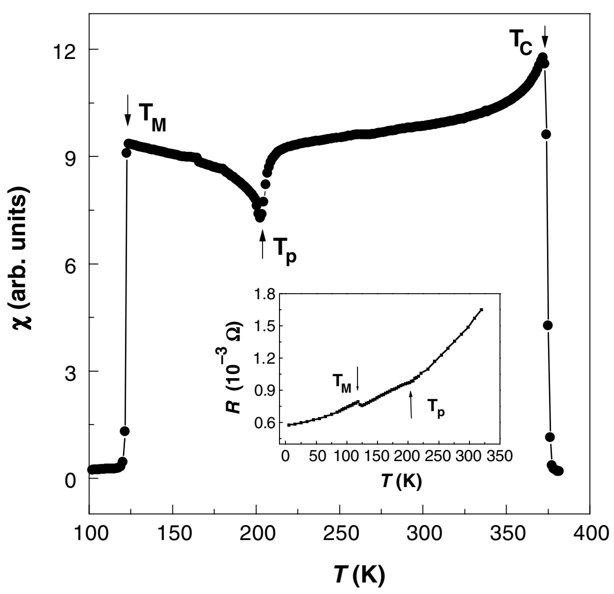

Figure 1. The temperature dependence of ac susceptibility χ measured upon cooling. The inset is the electrical resistance R as a function of temperature T upon cooling.

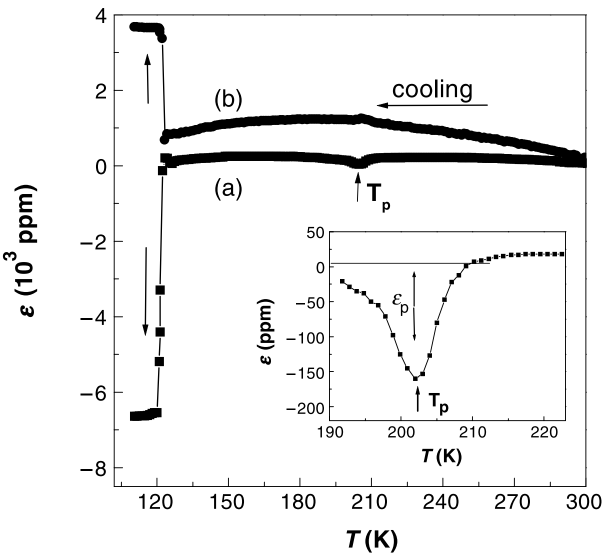

Figure 2. Strain–temperature (ε–T) curves of shape deformation measured along the [001] direction (curve (a)) and the [010] direction (curve (b)) in a free sample of the $Ni_{50.5}Mn_{24.5}Ga$ single crystals. The inset is a replot of ε in the [001] direction as a function of T at around 202 K for a better view.

Shown in figure 2 are the strain–temperature (ε–T) curves measured along the [001] and [010] directions of the parent phase in the cooling run, respectively, without an external applied bias field or a prestress. One can easy see that the martensitic transformation occurs at about 123 K and causes the sample to shrink about −0.62% in the longitudinal [001] direction, while the sample expands about 0.29% in its lateral [100] direction. Moreover, as marked by an arrow, a downward dip-like anomaly in the [001] direction is well above the martensitic transformation temperature T_M. A similar scene is in the [010] direction, but with a reversal and more small deformation. It is very interesting that in the same measuring direction, the strain sign of the premartensitic transition is completely consistent with that of the martensitic transformation. For a better view, the inset in figure 2 is a replot of ε in the [001] direction as a function of temperature T around 202 K. A dip-like peak is quite clearly observed, at about 202 K in the cooling run, which is an exact fit to the corresponding branch in the χ–T curve. Moreover, it is interesting to note that the premartensitic transition exhibits similar characteristics of the dip-like anomaly in the ε–T and in the χ–T curves; this suggests that the magnetic ordering stringently follows the crystal structure deformation. If the height of the dip-like anomaly (as marked in the inset in figure 2) is defined as the magnitude of the premartensitic transition strain (ε_p), one can clearly see that the premartensitic transition strain is very small, about $\varepsilon_p = -160$ ppm in the [001] direction, only 1/40 of the martensitic transformation strain in the same direction. As is well known, the premartensitic transition exhibits a pronounced temperature softening of the (1/3, 1/3, 0) phonon on the transverse TA_2 branch [3–6], and leads to the appearance of a micromodulated structure preceding the martensitic transformation [14]. The existence of the micromodulated structure can be explained as the result of the freezing of thermal vibrations of the soft TA_2 mode which become the static atomic displacements in this intermediate phase [14]. In general, in view of the crystallography, three directions of the cubic parent phase, [001], [010] and [100] should be equivalent to the lattice deformation during the premartensitic or martensitic transition. However, comparing the strain curve (a) with (b) in figure 2, one can see the apparent difference of strain scene. Furthermore, we found, as shown in figure 2, that the direction in which the premartensitic or martensitic strain shrink is always the [001], namely the growth direction of the single crystals. This implies that an intrinsic or technical factor might have been imposed on the sample, which induced the preferential orientation of the martensitic variants during the martensitic transformation and intervened the static atomic displacements accompanying with the soft mode condensation during the premartensitic transition. According to the previous work [17, 18], the residual internal stress, originating from the directional solidification during the Ni_2MnGa crystal growth process by the Czochralski method, can induce the preferential orientation of the martensitic variants and result in the largest shrinking strain along the growth direction. This behaviour of the internal stress is analogous to that of the uniaxial external stress on the Ni–Mn–Ga system [19]. In addition, Kokorin *et al* [14] reported an experimental investigation in which they observed a premartensitic transition strain during cooling of Ni_2MnGa elastically loaded at $T = 300$ K by a stress equal to above 17.6 MPa. Therefore, it is reasonable to believe that the shrinking strain of -160 ppm along the [001] direction at T_P in our present work is a result of the soft-mode condensation intervened by the residual internal stress.

Fixing the strain-measuring direction along the [001] direction, we have measured the temperature dependence of strain under various external dc magnetic fields. The measurements are performed during the cooling down process from room temperature and the sample is warmed in zero field each time from about 77 K. Figure 3 shows the evolution of strain around T_P upon cooling, with field of 0, 2 and 3 kOe applied along the [001] (a) and [010] (b) directions, respectively. The inset in figure 3(a) shows the relative orientation of the sample, measuring direction and applied magnetic field direction. One can easily see that an unambiguous decrease of T_P, accompanying with an obvious change of ε_p, with the increase of the magnetic field has been found. If we plot T_P as a function of applied magnetic field, as shown in figure 4, it is clear that T_P decreases monotonically with the increase of the applied field, and that with increasing magnetic field the T_P first decrease rapidly and then the decreasing rate becomes smaller and

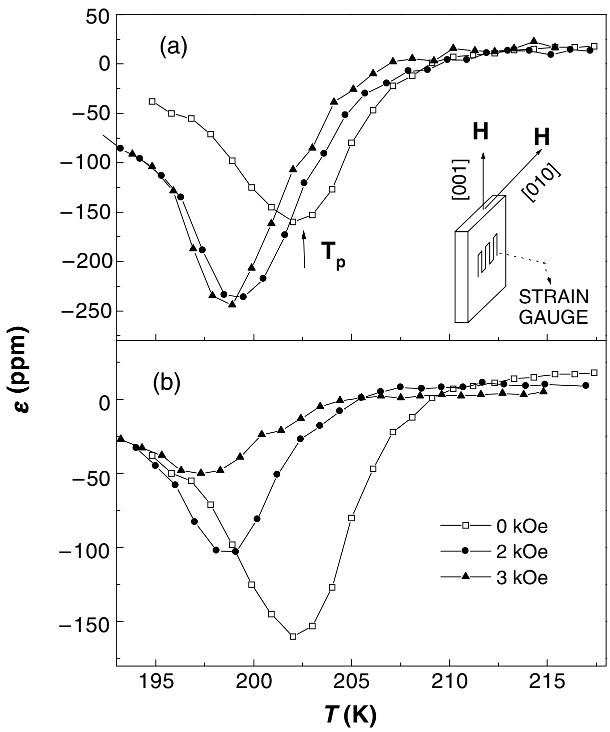

Figure 3. Strains ε as a function of temperature T across the premartensitic transition upon cooling for various dc magnetic fields; the inset in (a) shows the relative orientation of the sample, measuring direction and applied magnetic field direction.

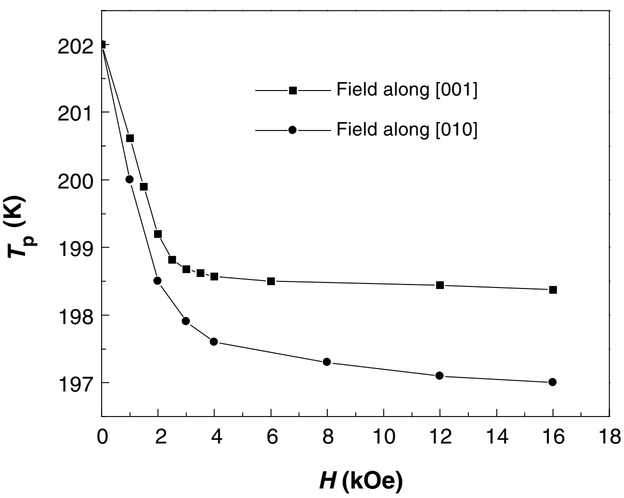

Figure 4. Premartensitic transition temperature T_P as a function of magnetic field H in the cooling run.

smaller. The T_P–H curves, at 2.5 and 3.5 kOe with field applied along the [001] and [010] directions, respectively, tend toward saturation, which is analogous to the scene measured by the application of a mechanical stress [20]. Such a saturated field of 3.5 kOe is less than that

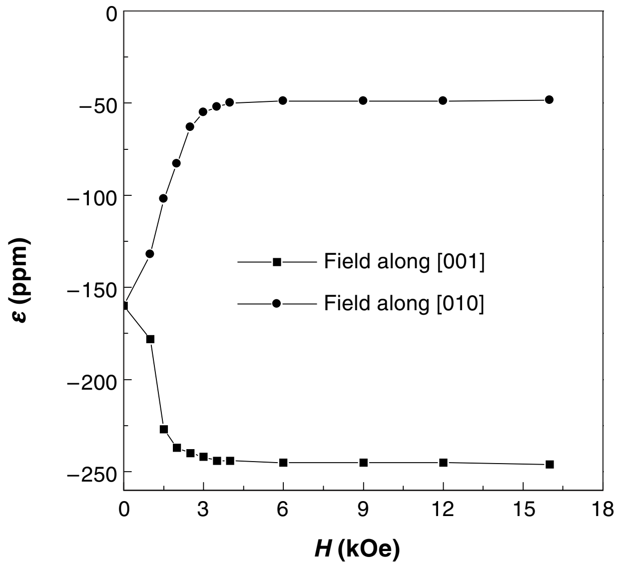

Figure 5. Premartensitic transition strain ε_P as a function of magnetic field H during the cooling process.

reported in the polycrystalline Ni_2MnGa samples [1, 9]. Moreover, it is noteworthy that the relative decrease of T_P for fields applied along the [010] direction is more pronounced than that of the [001] direction. In the [001] direction, the T_P value at 3 kOe is about 198.9 K, a decrease of 3.1 K from the T_P value at zero-field. However, in the [010] direction, the T_P value at 3 kOe is about 197.8 K, a decrease of 4.2 K from the T_P value at zero-field.

From the point of view of thermodynamics, the external magnetic field, like the temperature, is an independent variable that changes the free energy of the ferromagnetic material Ni_2MnGa system. When the external magnetic field is applied, the free energy of the premartensitic phase decreases mainly due to the increase of the Zeeman energy ($-\vec{M} \cdot \vec{H}$). Therefore, the applied magnetic field will increase T_P. The effect of the external magnetic field is analogous to the effect of hydrostatic pressure and external stress on the premartensitic transition in the Ni_2MnGa single crystals [10, 21]. On the other hand, according to a new Landau-type model [15], the premartensitic transition is a consequence of the magnetoelastic interaction between the phonon and the magnetization, and the magnetoelastic energy is quasilinear with M^2 (M represents magnetization) [9]. Thus, application of an external magnetic field will increase the alignment of the magnetic domains in the direction of the external magnetic field, which in turn will promote the magnetoelastic energy, and increase the magnetoelastic energy contribution. It is obvious that the increase of the magnetoelastic interaction will lead to a decrease of T_P due to the increase of free energy of the premartensitic phase. In fact, in the present study, T_P decrease with increasing field, suggesting that the magnetoelastic energy contribution to the free energy is the crucial term and determines the direction of the premartensitic transition temperature shift.

If we plot ε_P as a function of applied magnetic field, as shown in figure 5, one can see that the premartensitic transition deformation can be affected greatly by the bias magnetic field. The shrinking strain was promoted from −160 to −245 ppm in the measured direction of [001] with the increase of the field applied in the same direction from zero to 2.5 kOe. At about 2.5 kOe, the strain saturates. The net premartensitic transition strain enhanced by the saturated is about 85 ppm. Turning the field *laterally* applied to the [010] direction of the sample, however, the strain was suppressed by the field of 3.5 kOe from −160 to −50 ppm (relevant net strain induced by the field is 110 ppm), and shows a correspondingly larger saturated field of 3.5 kOe in the corresponding ε_p–H curve. Undoubtedly, this behaviour of the different strains should be related to the magnetoelastic interaction. That is, the application of the magnetic field will promote the magnetoelastic coupling. The increased magnetoelastic interaction will lead to an increase of transition strain, when the crystal lattice deformation induced by the magnetoelastic coupling is consistent with the intrinsic deformation. In contrast, it will lead to a decrease of the premartensitic transition strain. In addition, it should be noted that, when the magnetic field is applied along the same direction, the saturated field in T_P–H curves in figure 4 is completely consistent with the corresponding one in ε_p–H curves in figure 5. This indicates that the largest magnetoelastic interaction at T_P is attained when the strain is saturated.

Comas *et al* [10] performed an experimental investigation of the premartensitic transition in a Ni_2MnGa single crystal by the use of ultrasonic techniques. They have found that at room temperature all elastic constants (C', C_L and C_{44}), with increasing magnetic fields applied along the [100] and [110] directions, increase up to the same saturation value at about 1 and 3 kOe, respectively. Recently, the susceptibility measurement [8] in the stoichiometric Ni_2MnGa single crystal has found that, when an external field is biased along the different crystallographic directions, even at low field the decreasing rate of T_P is also different. They suggest that the magnetoelastic interaction depends on the direction of the applied field. In the present work, we found that T_P decreases more rapidly, and the net strain induced by the field is larger with the field applied along the [010] direction than with the field along the [001] direction. This further indicates that the magnetoelastic interaction in the $Ni_{50.5}Mn_{24.5}Ga_{25}$ single crystals is dependent on the direction of the field, even though the magnetic field is applied along the equivalent crystallographic directions. Because the premartensitic transition strains along the [001] and [010] directions in the free samples exhibit completely different deformation characteristics (as shown in figure 2), it is inevitable that anisotropy results between the two directions in the intermediate phase. Obviously, the emerging anisotropy between the [001] and [010] directions during the premartensitic transition is the origin of the above-mentioned dependence of the magnetoelastic interaction on the directions of magnetic field. In addition, it is worth pointing out that T_M is hardly changed for fields up to 16 kOe, which suggests that the magnetoelastic effect is absent or negligible at temperatures near the martensitic transformation temperature in the $Ni_{50.5}Mn_{24.5}Ga_{25}$ single crystals.

With the aim of pursuing the suggested anisotropy of the magnetoelastic coupling interaction between the [001] direction and the [010] direction, we have performed magnetization measurements at temperature T_P. Figure 6 shows the magnetization curves taken for the magnetic field applied along the [001] and [010] directions of the parent phase in the field range of interest. They indicate that the saturation magnetization is $\sigma_S = 69.4$ emu g^{-1}, and the magnetization of the [010] direction is slightly harder to saturate than that of the [001] direction in the premartensitic phase. Moreover, before reaching saturation, the Zeeman energy ($-\vec{M} \cdot \vec{H}$) for the field applied along the [001] direction is larger than that for the field applied along the [010] direction. As a result, the value of T_P is larger for the field applied along the [001] direction than along the [010] direction. However, if we consider qualitatively the dependence of T_P on M^2 before reaching saturation, one can easily find that T_P decreases significantly faster with field along the [010] direction than along the [001] direction, because there is the relative larger saturated field with magnetic field applied along the [010] direction. This suggests that the magnetoelastic interaction in the [010] direction is stronger than that in the [001] direction. Therefore, the origin of the different shape of the magnetization curves should be attributed to the different magnitude of magnetoelastic interaction in the [001] and [010] directions, and, due to the magnetoelastic interaction, the elastic energy stored by the

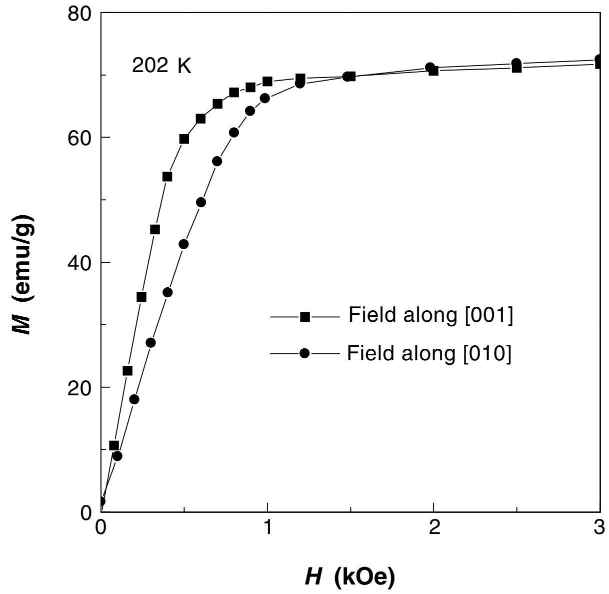

Figure 6. Magnetization M as a function of magnetic field H measured at T_P.

premartensitic transition gives rise to magnetic anisotropy, which dominates the magnetization processes. In addition, it is worth indicating that with the field applied along the same direction, the saturated field in the T_P–H curves in figure 4 or in the ε_p–H curves in figure 5 is larger than that in the M–H curves in figure 6. We argue this behaviour is a result of the fact that the intrinsic dynamical response of the bcc structure is modulated by the external static magnetic field, because the static magnetic field as an independent external variable not only restricts the alignment of the magnetic domains before the premartensitic transition, but also intervenes in the premartensitic transition during this transition process.

4. Conclusion

We have investigated the effect of magnetic fields on the premartensitic transition strain of a $Ni_{50.5}Mn_{24.5}Ga_{25}$ single crystals by measuring the strain across the premartensitic transition with various external dc magnetic fields applied along the [001] and [010] directions of the parent phase. It is found that the premartensitic transition temperature decreases monotonically with the increase of the applied field, and it decreases more rapidly with the field applied along the [010] direction than with the field applied along the [001] direction. Further, it is also found that the premartensitic transition deformation can be affected greatly by the biasing magnetic field. When the magnetic field is biased along the above-mentioned two directions, the premartensitic transition strain exhibits a different deformation scene and magnitude. The present results undoubtedly state a magnetoelastic interaction is responsible for the premartensitic transition, and the magnitude of the magnetoelastic interaction in the [010] direction is stronger than that in the [001] direction.

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References

[1] Yanwei Ma, Awaji S, Watanabe K, Matsumoto M and Kobayashi N 2000 *Appl. Phys. Lett.* **76** 37
[2] Fritsch G, Kokorin V V and Kempf A 1994 *J. Phys.: Condens. Matter* **6** L107
[3] Zheludev A, Shapiro S M, Wochner P, Schwartz A, Wall M and Tanner L E 1995 *Phys. Rev.* B **51** 11310
[4] Mañosa L, Planes A, Zarestky J, Lograsso T, Schlagel D L and Stassis C 2001 *Phys. Rev.* B **64** 24305
[5] Zheludev A, Shapiro S M, Wochner P and Tanner L E 1996 *Phys. Rev.* B **54** 15045
[6] Stuhr U, Vorderwisch P and Kokorin V V 2000 *J. Phys.: Condens. Matter* **12** 7541
[7] Mañosa L, Gonzàlez-Comas A, Obradó E and Planes A 1997 *Phys. Rev.* B **55** 11068
[8] Wang W H, Chen J L, Gao S X, Wu G H, Wang Z, Zheng Y F, Zhao L C and Zhan W S 2001 *J. Phys.: Condens. Matter* **13** 2607
[9] Zuo F, Su X and Wu K H 1998 *Phys. Rev.* B **58** 11127
[10] Gonzàlez-Comas A, Obradó E, Mañosa L, Planes A, Chernenko V A, Hattink B J and Labarta A 1999 *Phys. Rev.* B **58** 7085
[11] Stenger T E and Trivisonno J 1998 *Phys. Rev.* B **57** 2735
[12] Chernenko V A, Pons J, Segui C and Cesari E 2002 *Acta Mater.* **50** 53
[13] Castán T, Planes A and Saxena A 2003 *Phys. Rev.* B **67** 134113
[14] Kokorin V V, Chernenko V A, Cesari E, Pons J and Segui C 1996 *J. Phys.: Condens. Matter* **8** 6457
[15] Planes A, Obradó E, Gonzàlez-Comas A and Mañosa L 1997 *Phys. Rev. Lett.* **79** 3926
[16] Castán T, Vives E and Lindgård P A 1999 *Phys. Rev.* B **60** 7071
[17] Wang W H, Wu G H, Chen J L, Yu C H, Wang Z, Zheng Y F, Zhao L C and Zhan W S 2000 *J. Phys.: Condens. Matter* **12** 6287
[18] Wang W H, Wu G H, Chen J L, Yu C H, Gao S X, Zhan W S, Wang Z, Gao Z Y, Zheng Y F and Zhao L C 2000 *Appl. Phys. Lett.* **77** 3245
[19] Martynov V V and Kokorin V V 1992 *J. Physique* III **2** 739
[20] Mañosa L, Gonzàlez-Comas A, Obradó E and Planes A 1999 *Mater. Sci. Eng.* A **273–275** 329
[21] Chernenko V A and L'vov V A 1996 *Phil. Mag.* A **73** 999