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Premartensitic transition in $Ni_{2+x}Mn_{1-x}Ga$ Heusler alloys

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Abstract

The temperature dependencies of the resistivity and magnetization of a series of $Ni_{2+x}Mn_{1-x}Ga$ ($x = 0$–0.09) alloys were investigated. Along with the anomalies associated with ferromagnetic and martensitic transitions, well-defined anomalies were observed at the temperature of premartensitic transformation. The premartensitic phase existing over the temperature range 200–260 K in the stoichiometric Ni_2MnGa is progressively suppressed by the martensitic phase with increasing Ni content and has vanished in the $Ni_{2.09}Mn_{0.91}Ga$ composition.

1. Introduction

In Ni_2MnGa, like in many other Heusler alloys containing manganese, the indirect exchange interaction between magnetic ions results in ferromagnetism which is usually described in terms of the local magnetic moment at the Mn site [1]. For the stoichiometric Ni_2MnGa a structural transition of the martensitic type from the parent cubic to a complex tetragonally based structure occurs at $T_M = 202$ K while ferromagnetic ordering sets in at $T_C = 376$ K [2]. The martensitic transition temperature T_M was found to be sensitive to the composition, and values of T_M between 175 and 450 K have been reported. A specific feature of the Ni–Mn–Ga system is that in alloys with a high T_M (>270 K) a number of intermartensite transformations can be induced by an external stress [3, 4], whereas in the alloys with lower T_M the martensitic transition is preceded by a weakly first-order premartensitic phase transition [5–8]. Inelastic neutron scattering experiments [9] performed on stoichiometric Ni_2MnGa showed the existence of a soft $[\xi\xi 0]TA_2$ phonon mode over a wide temperature interval, which is common to martensitic alloys with bcc structure. An important observation in these measurements was that the TA_2 phonon branch at a wave vector of $\xi_0 \approx 0.33$ incompletely condenses at the premartensitic transition temperature, $T_P \approx 260$ K, well above the martensitic transition temperature,

$T_M = 220$ K. On cooling from T_P to T_M, the frequency of the soft mode increases. This would suggest that the soft-mode formation is associated with the premartensitic phase transformation rather than with the martensitic one. By transmission electron microscopy observation [10] it was established that the premartensitic phase consists of a micromodulated 'tweed' structure without macroscopic tetragonal distortions, so the parent cubic symmetry is preserved. The modulation of the premartensitic phase was found to correspond to the wave vector $\xi_0 \approx 0.33$.

It is necessary to stress that although no premartensitic transition was found in compositions with high T_M, the precursor phenomenon (softening of the $[\xi\xi 0]\mathrm{TA}_2$ phonon branch at the wave vector $\xi_0 \approx 0.33$) has been clearly observed by means of inelastic neutron scattering [11, 12]. Except for the partial condensation of the TA_2 phonon branch observed by Zheludev *et al*, the only essential difference between the inelastic neutron scattering results obtained for three samples of different stoichiometry [9, 11, 12] is that the width in ξ where softening occurs becomes broader as T_M increases [13].

At present, the reason that the premartensitic transformation is observed only in the alloys with $T_M \leqslant 260$ K seems to be unclear. There is strong evidence [5, 7, 11] that the magneto-elastic interaction plays a crucial role in the formation of the premartensitic phase. Also, the theoretical investigation [8] predicts that the premartensitic transition is observed only in the case of large values of the magneto-elastic coupling parameter. From the results of magnetic and transport measurements on several near-stoichiometric $\mathrm{Ni}_{2-x}\mathrm{Mn}_{1+x}\mathrm{Ga}$ samples [14] it can be concluded that the premartensitic transition is less sensitive to the change of composition than the martensitic one. This gives grounds for suggesting that a deviation from the stoichiometry can lead to the disappearance of the premartensitic transition for some critical composition.

The importance of the conduction electron density in stabilizing the Heusler structure was noted long ago and, in particular, it was suggested [15] that the structure is stabilized because the Fermi surface touches the Brillouin zone boundary. If this is the case, a partial substitution of Mn for Ni in $\mathrm{Ni}_{2+x}\mathrm{Mn}_{1-x}\mathrm{Ga}$ alloys resulting in an increase of the conduction electron density should increase the martensitic transition temperature. This makes it possible to determine the compositional dependencies of T_M and T_P. For this purpose we have studied temperature dependencies of the electrical resistivity and magnetization in $\mathrm{Ni}_{2+x}\mathrm{Mn}_{1-x}\mathrm{Ga}$ alloys in which Mn is partially substituted for Ni in the range $x = 0$–0.09.

2. Sample preparation and measurements

Polycrystalline $\mathrm{Ni}_{2+x}\mathrm{Mn}_{1-x}\mathrm{Ga}$ ingots were prepared by a conventional arc-melting method in an Ar atmosphere. The ingots were homogenized in vacuum at 1100 K for nine days and slowly cooled down. Room temperature x-ray diffraction showed the single-phase cubic structure of the alloys. The samples for the resistivity and magnetization measurements were spark cut from the ingots and were of dimensions $0.6 \times 1 \times 6$ mm^3. The electrical resistivity was measured in the temperature range 100–450 K by the ac four-terminal method. Magnetic measurements were made using a SQUID magnetometer.

3. Experimental results and discussion

The temperature dependencies of resistivity ρ measured during cooling in $\mathrm{Ni}_{2+x}\mathrm{Mn}_{1-x}\mathrm{Ga}$ ($x = 0$–0.09) are shown in figure 1. Except for the $\mathrm{Ni}_{2.09}\mathrm{Mn}_{0.91}\mathrm{Ga}$ composition, the $\rho(T)$ dependencies of the other samples exhibit three well-defined anomalies at temperatures corresponding to the ferromagnetic (T_C), premartensitic (T_P) and martensitic (T_M) transitions. With deviation from the stoichiometry, the change in slope of the curve related to the

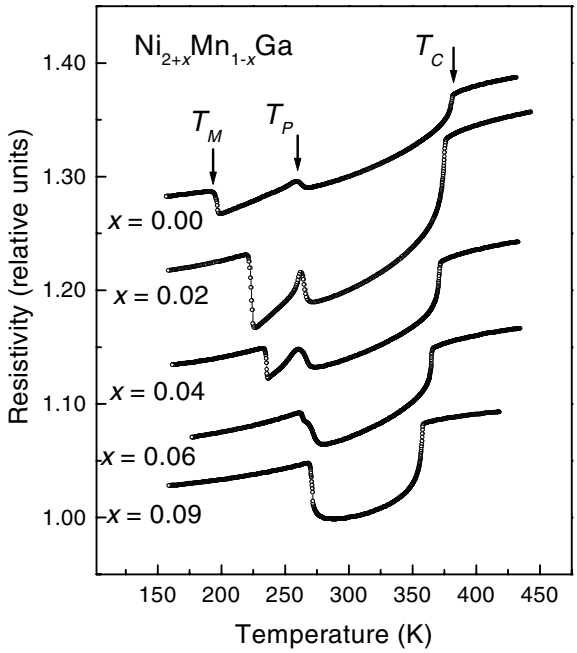

Figure 1. Temperature dependencies of the electrical resistivity in $Ni_{2+x}Mn_{1-x}Ga$ ($x = 0$–0.09).

ferromagnetic transition shifts to lower temperatures, and the jump-like behaviour of ρ related to the martensitic transformation shifts to higher temperatures. This decrease of T_C and increase of T_M with increasing Ni content is in good agreement with [16]. However, the temperature dependence of the resistivity and especially anomalies at the transformation temperatures differ significantly from the previously published results [14, 16, 17]. Indeed, it has been reported that in the stoichiometric and near-stoichiometric Ni–Mn–Ga alloys the martensitic transition is accompanied by a weak change in the slope of the resistivity curve, whereas the change in the slope of the curve at the ferromagnetic transition is more pronounced. In our case there is a marked jump-like behaviour of the resistivity at T_M for all the compositions studied. The anomaly at the ferromagnetic transition temperature T_C also looks quite different from an anomaly typically observed at T_C in this Heusler alloy, and instead of the smooth decrease of the resistivity reported in [16, 17] we observed a sharp drop in the resistivity when ferromagnetic order sets in at T_C. Finally, in the present measurements a prominent anomaly at the premartensitic transition has been observed for the first time. It could be suggested that the origins of these major differences between the present and previously published results [14, 16, 17] for $\rho(T)$ lie either in the thermal treatment procedure or in the room temperature aging of the alloys. As has been mentioned above, the samples used in this study were annealed for nine days at 1100 K and slowly cooled to room temperature. Our previous studies of the $Ni_{2+x}Mn_{1-x}Ga$ ($x = 0$–0.19) series [16] were done on samples which were quenched in ice water after a nine-day annealing at 1100 K. So it could be the case that heat treatment significantly influences scattering mechanisms for conduction electrons in $Ni_{2+x}Mn_{1-x}Ga$ alloys. However, in our opinion it is more likely that the origin of these differences lies in the room temperature aging of $Ni_{2+x}Mn_{1-x}Ga$. While the present data were obtained within a week after annealing, in the previous case [16] the samples had been aged for six months at room temperature before the measurements were carried out. Thus, it

seems plausible that the results of the resistivity measurements presented in [16] differ from the present results due to this long-term aging.

As is seen from figure 1, the resistivity demonstrates either a well-defined peak ($x = 0$–0.04 compositions) or a two-step-like behaviour ($x = 0.06$–0.08 compositions) at the temperature T_P. The premartensitic transition temperature T_P was determined either as that of the peak or as that of the bend of the two-step-like resistivity curve. Unlike T_C and T_M, the premartensitic transition temperature T_P does not shift with Ni excess and T_P ($\approx$260 K) remains essentially the same for all alloys in the range of compositions studied (figure 2). Because of the hysteretic behaviour of the martensitic transition, the compositional phase diagram shown in figure 2 is constructed for the cooling process.

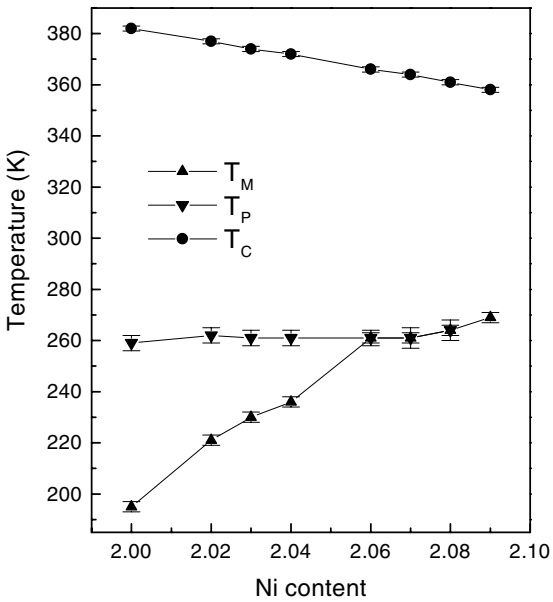

Figure 2. Temperatures of the ferromagnetic (T_C), premartensitic (T_P) and martensitic (T_M) phase transitions as a function of Ni content in the $Ni_{2+x}Mn_{1-x}Ga$ alloys.

For the compositions with low Ni content, T_M and T_P are well separated and the premartensitic transition manifests itself as a well-defined peak in the resistivity curve. Increasing Ni content results in enhancement of T_M and, as a consequence, only the right-hand (high-temperature) part of the peak is present in $\rho(T)$ for the $x = 0.06$–0.08 compositions (figure 1). The left-hand (low-temperature) part of the peak may not be detectable in the martensitic phase because all of the physical characteristics of the materials (crystal structure, Fermi surface, mean free path and so on) change drastically upon martensitic transformation. It is also interesting to compare the behaviour of the resistivity at T_M and T_P measured during heating and cooling for $Ni_{2.04}Mn_{0.96}Ga$ and $Ni_{2.08}Mn_{0.92}Ga$ (figure 3). In the case of $Ni_{2.04}Mn_{0.96}Ga$, the resistivity shows a significant temperature hysteresis at T_M whereas the temperature hysteresis at T_P is small, which is in agreement with published results [5, 7, 9]. For $Ni_{2.08}Mn_{0.92}Ga$ the two-step-like anomaly observed during cooling completely disappears upon warming up, and the resistivity smoothly decreases down to the extreme value. Moreover, the hysteretic feature seen in the upper part gradually narrows and vanishes in the lower part. This demonstrates that the observed two-step-like behaviour of the resistivity is not a peculiar feature of the martensitic transition for the $x = 0.06$–0.08 compositions, but is the outcome of

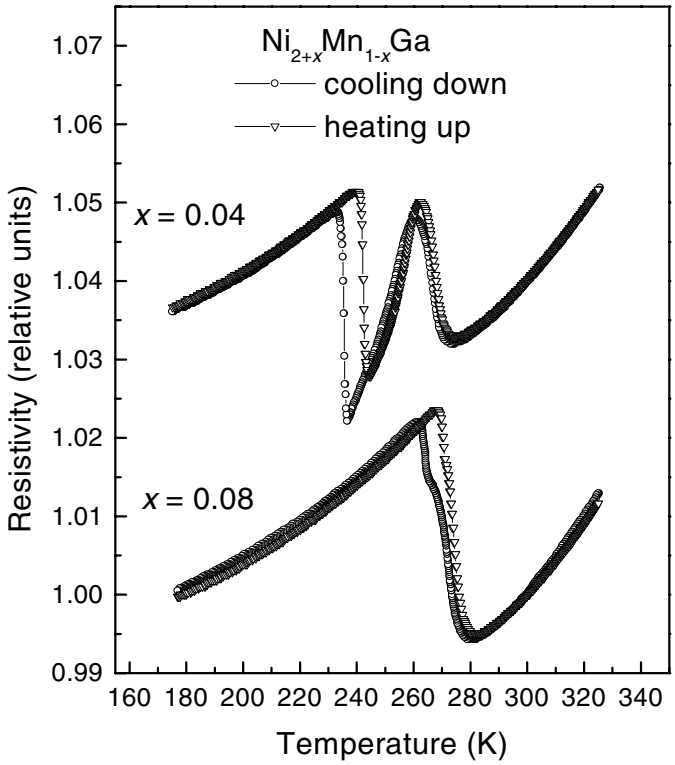

Figure 3. Features of $\rho(T)$ at martensitic and premartensitic transitions in $Ni_{2.04}Mn_{0.96}Ga$ and $Ni_{2.08}Mn_{0.92}Ga$ upon cooling and heating.

simultaneously occurring premartensitic and martensitic transitions. The anomaly in resistivity corresponding to T_P had been completely taken up by the martensitic phase for the highest-Ni-content composition in the series, $Ni_{2.09}Mn_{0.91}Ga$, and the resistivity shows only two anomalies corresponding to the ferromagnetic and martensitic phase transitions (figure 1). In our opinion, these findings are consistent with absence of the premartensitic transition in Ni–Mn–Ga alloys with a high martensitic transition temperature T_M [11, 12].

The temperature dependencies of the magnetization M measured in a 100 Oe magnetic field also showed clear anomalies at T_P in the $x = 0$–0.04 composition range. However, such anomalies were not observed, either upon cooling or upon heating, for the range of compositions $x = 0.06$–0.08. In fact, the absence of them during warming agrees with the corresponding resistivity data. Since for the $x = 0.06$–0.08 compositions the martensitic and premartensitic transitions merge, anomalies of M related to T_P are not observed upon cooling probably because they are masked by the drastic decrease of M occurring at the martensitic transformation. An example of $M(T)$ dependence for the compositions with separated T_P and T_M is shown in figure 4. $M(T)$ revealed a pronounced dip in magnetization of the sample at T_P. The drastic decrease in magnetization at $\approx$227 K, shown in the inset of figure 4, is common for transformations from ferromagnetic austenite to ferromagnetic martensite in Ni–Mn–Ga alloys and will not be discussed here. The temperature of the premartensitic transition T_P is equal to 262 K, which is in excellent agreement with the corresponding resistivity data. Instead of a smooth diminution of the magnetization at T_M, the premartensitic transition is attended by a complicated behaviour of the magnetization. The rapid decrease of magnetization in

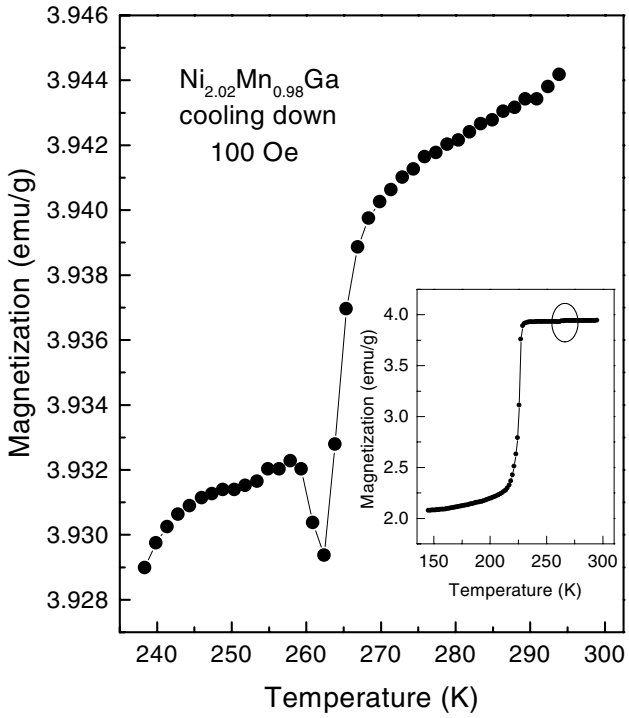

Figure 4. The temperature dependence of the magnetization M in $Ni_{2.02}Mn_{0.98}Ga$ in the vicinity of the premartensitic transition. The inset shows $M(T)$ over the entire temperature interval.

the temperature interval from 268 to 262 K could be a consequence of the freezing of the atomic displacements related to the soft $\frac{1}{3}[110]$ phonon mode. In this case the appearance of modulations of the cubic phase results in an increase of magnetic anisotropy which explains the drop in magnetization. The upturn in magnetization at temperatures below $T_P = 262$ K is presumably due to the ordering of the premartensitic phase. This suggestion is consistent with the evolution of the Bragg peak at $\boldsymbol{q} = (\frac{1}{3}\frac{1}{3}0)$ [9] and the results of ultrasonic measurements [6], which clearly demonstrated that the premartensitic phase becomes fully developed and ordered at temperatures below T_P.

The martensitic transformation in Ni–Mn–Ga alloys is believed to occur due to the contact between the Fermi surface and a Brillouin zone boundary [2]. In this sense the compositional dependence of T_M in $Ni_{2+x}Mn_{1-x}Ga$ can be understood as resulting from a change of the Fermi energy due to the increase in the conduction electron concentration upon substitution of Mn for Ni. On the other hand, it has been suggested [9] that the origin of the premartensitic transition lies in specific nesting features of the multiply connected Fermi surface. The effect of uniaxial stress [18] on the anomalous phonon branch in Ni_2MnGa results in the shifting of the phonon anomaly and the premartensitic transition temperature T_P to higher q-values and temperatures. External stress can actually change the geometry of the Fermi surface and modifies the nesting vector. The fact that T_P does not depend on x in $Ni_{2+x}Mn_{1-x}Ga$ alloys means presumably that the increase in the conduction electron concentration does not affect this particular part of the Fermi surface significantly.

Summarizing our speculation regarding the compositional dependence of the martensitic and premartensitic phase transitions, we argue that the premartensitic phase is suppressed by

the martensitic phase with deviation from the stoichiometry in $Ni_{2+x}Mn_{1-x}Ga$ alloys. The premartensitic transition couples with the martensitic transition in the range of x from 0.06 to 0.08 and completely vanishes at 264 K for the critical composition $x = 0.09$ of $Ni_{2+x}Mn_{1-x}Ga$ alloys. However, we do not rule out the possibility that the premartensitic transition gives rise to an intermartensitic transition in alloys with higher Ni content. In fact, such a possibility has been mentioned in [7], where the authors analyse data collected from the literature for a broad range of Ni–Mn–Ga compositions. In view of this, it is also worth mentioning that in a simpler classification the experimentally observed modulations of the martensitic phase in Ni–Mn–Ga alloys correlate with the temperature of the martensitic transition T_M as follows [19]: five-layered martensite is observed in alloys with $T_M < 270$ K, whereas alloys with $T_M > 270$ K exhibit seven- or ten-layered martensitic structures. This characteristic martensitic transition temperature, $T_M = 270$ K, where the modulation of the martensitic phase changes from five to seven (or ten) layers accords well with the critical temperature $T_P = 264$ K at which the premartensitic phase vanishes determined in our experiments.

Very recently [20] a phenomenological theory of structural and magnetic phase transitions in $Ni_{2+x}Mn_{1-x}Ga$ alloys which takes into account strain, crystal lattice modulation, magnetic order parameter and interaction between these subsystems has been developed. It has been shown that the addition of an order parameter ψ accounting for the crystal lattice modulation of the premartensitic phase to the general expression for the free energy [16] leads to an intermartensitic transition. In the compositional phase diagram this transition results from an extension of the line of the premartensitic transition into the martensitic phase. The results of numerical calculations indicate that the premartensitic transition temperature as a function of concentration in $Ni_{2+x}Mn_{1-x}Ga$ alloys intersects the line of the martensitic phase transition at $x \sim 0.11$. This agrees fairly well with the experimental value $x = 0.09$.

4. Conclusions

In conclusion, the most novel and significant findings of our experiments are that the premartensitic phase is progressively suppressed by the martensitic phase until it completely vanishes for the critical composition $Ni_{2.09}Mn_{0.91}Ga$ at 264 K. Assuming that the features of the Fermi surface suggested in [2] and [9] are responsible for T_M and T_P, this means that the increase in the conduction electron density does not modify the nesting vector and mainly affects the Fermi energy.

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References

[1] Plogmann S, Schlatholter T, Braun J, Neumann M, Yarmoshenko Yu M, Yablonskikh M V, Shreder E I, Kurmaev E Z, Wrona A and Slebarski A 1999 *Phys. Rev.* B **60** 6428
[2] Webster P J, Ziebeck K R A, Town S L and Peak M S 1984 *Phil. Mag.* B **49** 295
[3] Martynov V V and Kokorin V V 1992 *J. Physique* III **2** 739
[4] Vasil'ev A N, Kaiper A, Kokorin V V, Chernenko V A, Takagi T and Tani J 1993 *JETP Lett.* **58** 306
[5] Planes A, Obrado E, Gonzalez-Comas A and Manosa L 1997 *Phys. Rev. Lett.* **79** 3926

[6] Stenger T E and Trivisonno J 1998 *Phys. Rev.* B **57** 2735
[7] Gonzalez-Comas A, Obrado E, Manosa L, Planes A, Chernenko V A, Hattink B J and Labarta A 1999 *Phys. Rev.* B **60** 7085
[8] Castan T, Vives E and Lindgard P-A 1999 *Phys. Rev.* B **60** 7071
[9] Zheludev A, Shapiro S M, Wochner P, Schwartz A, Wall M and Tanner L E 1995 *Phys. Rev.* B **51** 11 310
Zheludev A, Shapiro S M, Wochner P and Tanner L E 1996 *Phys. Rev.* B **54** 15 045
[10] Cesari E, Chernenko V A, Kokorin V V, Pons J and Segui C 1997 *Acta Mater.* **45** 999
[11] Stuhr U, Vorderwisch P, Kokorin V V and Lindgard P-A 1997 *Phys. Rev.* B **56** 14 360
[12] Stuhr U, Vorderwisch P and Kokorin V V 2000 *J. Phys.: Condens. Matter* **12** 7541
[13] Very resent results:
Manosa L *et al* 2001 *Phys. Rev.* B **64** 024305
suggest that for the composition with close martensitic and ferromagnetic transition temperatures the dip is located at a lower ξ-value, $\xi \approx 0.25$, although the maximum softening takes place at $\xi \approx 0.33$.
[14] Zuo F, Su X, Zhang P, Alexandrakis G C, Yang F and Wu K H 1999 *J. Phys.: Condens. Matter* **11** 2821
[15] Smit J 1978 *J. Phys. F: Met. Phys.* **8** 2139
[16] Vasil'ev A N, Bozhko A D, Khovailo V V, Dikshtein I E, Shavrov V G, Buchel'nikov V D, Matsumoto M, Suzuki S, Takagi T and Tani J 1999 *Phys. Rev.* B **59** 1113
[17] Chernenko V A 1999 *Scr. Mater.* **40** 523
[18] Zheludev A and Shapiro S M 1996 *Solid State Commun.* **98** 35
[19] Pons J, Chernenko V A, Santamarta R and Cesari E 2000 *Acta Mater.* **48** 3027
[20] Buchel'nikov V D, Zayak A T, Vasil'ev A N and Takagi T 2000 *Int. J. Appl. Electromagn. Mech.* **12** 19