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Elastic properties of NiTi

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Abstract. We present measurements of the elastic constants on a single crystal of the shape-memory alloy NiTi in a wide temperature range. Step-like anomalies and hysteresis are detected at the austenitic–martensitic phase transition which provide evidence for the strain–order parameter coupling in the pre-martensitic phases. The results are discussed in the framework of existing Landau theory models.

1. Introduction

NiTi belongs to a class of metallic alloys exhibiting the shape-memory effect. The physical properties of this material such as electrical resistivity, magnetic susceptibility, internal friction, specific heat, linear expansion and optical properties have been extensively studied [1] (for a review see [2]). A microscopic theory of the shape-memory effect is still elusive. This remarkable phenomenon seems to be related to a series of structural phase transitions depending strongly on composition [2]. As far as the elastic properties of NiTi are concerned earlier incomplete measurements of the elastic constants of single crystals exhibited anomalies in the transverse modes [3, 4] and in the polycrystalline material a minimum in the longitudinal and transverse modes [5]. The behaviour of elastic constants at the phase transition can be a valuable clue for a more detailed theoretical description. These data are particularly important for the relevant parameters of phenomenological Ginzburg–Landau theories that have been developed [6, 7].

It has been established that the near-equiatomic NiTi transforms from a high-temperature β-phase of cubic $Pm3m$ symmetry (CsCl structure) via intermediate so-called pre-martensitic phases to a low-temperature martensitic phase of monoclinic $P2_1/m$ symmetry [8]. The transition to the intermediate SL phase (superlattice-phase) starts at $T = S_s$ when the three-fold superstructure is established as a second-order displacive phase transition caused by a condensing soft-mode T_2A phonon at $q_1 = \frac{1}{3}\langle 110\rangle 2\pi/a$ as detected by neutron scattering experiments [9, 10]. Another transition to an intermediate phase of rhombohedral symmetry (R phase) starting at $T = R_s$ is of first order [10]. The transition to the final martensitic state is again a first-order transition [9]. It is characterized by the starting and finishing temperatures M_s and M_f respectively. The first-order phase transitions exhibit hysteresis. Upon heating the multidomain martensitic phase retransforms directly to the initial single-crystal

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orientation of the β-phase characterized by the starting and finishing temperatures A_s and A_f respectively [10].

In this article we present a thorough study of all elastic constants resulting from ultrasonic velocity measurements performed on a high-quality single crystal of $Ni_{50.5}Ti_{49.5}$. We detect strong anomalies with an unprecedented magnitude in all elastic constants. Our measurements of the absolute values of the elastic constants confirm earlier results for some modes obtained by similar experimental techniques but exhibit a smaller value for the longitudinal elastic constant $(c_{11} + c_{12} + 2c_{44})/2$ compared with neutron scattering results.

2. Experimental setup

2.1. Crystal growth and characterization

The $Ni_{50.5}Ti_{49.5}$ single crystals have been grown by a Czochralski technique from a levitated melt of a $Ni_{50}Ti_{50}$ composition using a cold crucible. The constituent metals Ni and Ti, both of 4N5 purity, were brought to reaction and homogenized in a cold crucible before crystal growth. Preparation and crystal growth were performed under a 3 bar argon (6N) atmosphere. The pulling speed was 3 mm h^{-1} with no rotation. A single crystal of NiTi was used to seed the mixture. After growth the boules were cooled rapidly. Single crystals of a volume up to 1 cm^3 have been obtained and cut from the boules by spark erosion. The stoichiometric composition of the crystals were analysed using x-ray fluorescence. NiTi boules which were homogenized by levitation melting and quenched were used as standards. From our analysis we conclude that the congruent composition is not equiatomic NiTi [11] but $Ni_{50.6}Ti_{49.4}$. The composition of the measured crystal is $Ni_{50.5}Ti_{49.5}$ yielding a density of 6.46×10^3 kg m^{-3}. The mosaic spread of our high-quality single crystal is 0.2°.

2.2. Measurements of elastic constants

The ultrasonic measurements have been performed by a phase sensitive RF pulse echo method achieving a resolution of the relative sound velocity change of up to a few parts in 10^6 [12]. Values of absolute sound velocities can be determined with an accuracy of approximately 2%. For the sound wave generation and detection piezoelectric transducers of quartz and $LiNbO_3$ as well as aluminated piezoelectric films have been employed. In the temperature range below 270 K transducers were bonded with Thiokol LP 32 or a two component epoxy glue. The measurements in the range from 250 to 480 K were accomplished with the bonding agent Dow Corning 806a, allowing us to heat or cool beyond the endpoints of the hysteretic phase transition. These measurements were performed in a Lindberg heavy-duty tube furnace with nitrogen gas cooling. The dimensions of the sample are 4.61 mm × 2.7 mm × 2.4 mm. Electrical resistance measurements were performed by a four-point DC method on rods of 10 mm length and 0.5 mm^2 cross section with an accuracy of 8%.

3. Experimental results

In the β-phase the elastic properties of NiTi are described by three independent elastic constants. Due to the (110), $(1\bar{1}0)$ and (001) surfaces of the single crystal we could

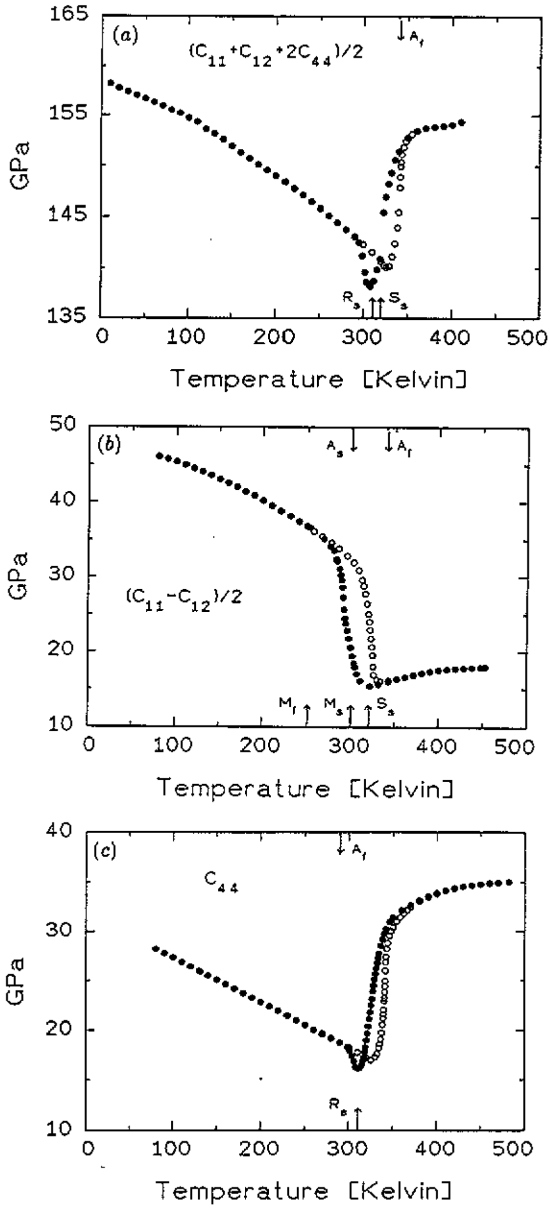

Figure 1. Temperature dependence of the elastic constants of $Ni_{50.5}Ti_{49.5}$: (*a*) longitudinal mode $(c_{11}+c_{12}+2c_{44})/2$; (*b*) transverse mode $(c_{11}-c_{12})/2$; and (*c*) transverse mode c_{44}. Full and open circles represent the cooling and heating cycle, respectively. The phase transition temperatures indicated by arrows are discussed in the text. Those below (above) the curves are relevant for the cooling (heating) cycle only.

measure the two shear modes $(c_{11}-c_{12})/2$ and c_{44} as well as the longitudinal mode $(c_{11}+c_{12}+2c_{44})/2$. Figure 1 shows their temperature dependence.

The low value of the transverse $(c_{11}-c_{12})/2$ mode and its further softening as the phase transition is approached from above is typical for martensitic phase transformations. We also note the low value and the softening of c_{44} (see figure 1(*c*)) leading to the lowest elastic anisotropy $A = 2c_{44}/(c_{11} - c_{12}) \simeq 2$ of all known shape-memory alloys [13]. Figure 2 shows how the elastic anisotropy stays nearly constant upon cooling and decreases rapidly at the β-phase–martensite transition to approximately $A \simeq 0.6$. The minimum of the elastic anisotropy near $R_s = 310$ K is a consequence of the behaviour of c_{44} which will be discussed later. Table 1 allows a comparison of our absolute values of the elastic constants with those measured using a composite piezoelectric vibrator technique [4], ultrasound velocity measurements [3] and neutron scattering experiments [13]. The neutron scattering measurements and our measurements were performed on crystals of the same composition. Figure 3 shows the electrical resistance of $Ni_{50.5}Ti_{49.5}$ as a function of temperature. The arrows in all figures indicate the characteristic temperatures for the phase transitions found by the neutron scattering experiments [13].

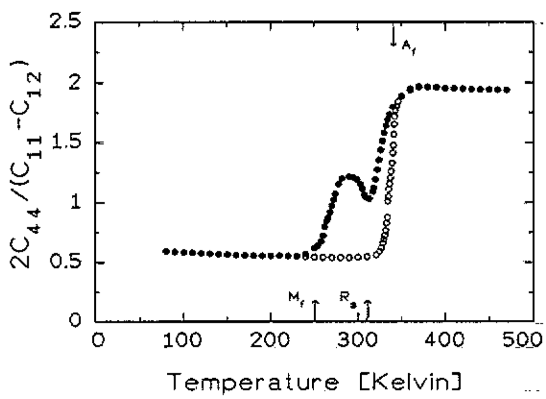

Figure 2. Temperature dependence of the elastic anisotropy $A = 2c_{44}/(c_{11} - c_{12})$ of $Ni_{50.5}Ti_{49.5}$. Full and open circles represent the cooling and heating cycle, respectively. The phase transition temperatures indicated by arrows are discussed in the text. Those below (above) the curves are relevant for the cooling (heating) cycle only.

As the temperature decreases towards the martensitic phase transition all elastic constants exhibit an increasing softening merging into a step-like behaviour which occurs near the appearance of the soft-mode induced SL phase at $S_s = 320$ K as determined by the neutron scattering experiments [13]. However while the modes $(c_{11}+c_{12}+2c_{44})/2$ and c_{44} exhibit a sharp decrease of 10% and 50% respectively there is an inverted behaviour of $(c_{11} - c_{12})/2$ with an increase of 100% at the beginning of the actual martensitic phase transition at $M_s = 300$ K. We continue to label the elastic constants as before but one has to realize that the crystal structure of the low-temperature phase is monoclinic and the crystal exhibits strong twinning [9].

Upon further cooling, the elastic constants show a nearly linearly increasing behaviour in the multidomain phase. Below $M_f = 250$ K the phase transformation is considered complete as suggested by the resistance measurements (see figure 3) and neutron scattering experiments [13]. Heating from this point, the elastic constants exhibit a hysteretic behaviour at the phase transition with an offset of 15 to 25 K. The β-phase transition starts at $A_s = 300$ K. Above 360 K all elastic constants and the resistance retrace their high-temperature paths while the neutron scattering experiments indicate a transition endpoint of $A_f = 340$ K [13]. One notes that the

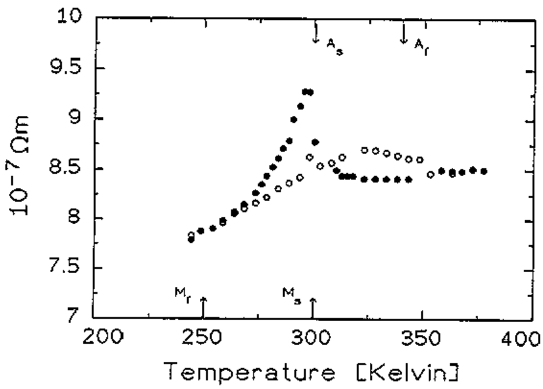

Figure 3. Temperature dependence of electrical resistance of $Ni_{50.5}Ti_{49.5}$. The phase transition temperatures indicated by arrows are discussed in the text. Those below (above) the curves are relevant for the cooling (heating) cycle only.

anomaly of the elastic constant c_{44} in comparison with the heating cycle is enhanced upon cooling (see figure 1(*c*)). According to the neutron scattering experiments the minimum at $R_s = 310$ K corresponds to the appearance of the rhombohedral phase. The behaviour of the elastic constant $(c_{11} + c_{12} + 2c_{44})/2$ also reflects this anomaly of c_{44}. Upon heating, the acoustic damping decreases typically as the martensite–β-phase transition is terminated. This is clearly related to the vanishing domain wall stress effects in the high-temperature cubic phase. At higher temperatures, however, deteriorating bond quality usually leads to increased damping and finally to a loss of the signal.

From our measurements the cubic bulk modulus $c_B = (c_{11} + 2c_{12})/3$ yields a value of $c_B = 114$ GPa at 400 K. In the temperature dependence of the bulk modulus we find a small peak at $S_s = 320$ K upon cooling and at $A_f = 340$ K upon heating. Below the phase transition c_B is nearly constant. The cubic Poisson ratio $\nu = c_{12}/(c_{11} + c_{12})$ exhibits a step-like behaviour from $\nu \simeq 0.43$ at 400 K to $\nu \simeq 0.35$ below the phase transition.

4. Discussion

The instability of BCC structures with respect to simple $\langle 110\rangle$, $\langle 1\bar{1}0\rangle$ shear is reflected in the low value and temperature dependence of the elastic constant $(c_{11} - c_{12})/2$ [14] as is also observed in our results (figure 1(*b*)). In the framework of the Landau theory the softening of the elastic constant $(c_{11} - c_{12})/2$ can be described by a coupling of the symmetry strain $\epsilon_s = \epsilon_{xx} - \epsilon_{yy}$ to the condensing T_2A phonon mode at $q_1 = \frac{1}{3}\langle 110\rangle 2\pi/a$ leading to the pre-martensitic SL phase at $S_s = 320$ K. This phonon-mode with wavevector q_1 and displacement vector u along $\langle 110\rangle$ and $\langle 1\bar{1}0\rangle$, respectively, has the same symmetry as the ultrasonic shear-wave. The lattice displacement amplitude $\langle u\rangle$ can be taken as a Landau order parameter η which exhibits a mean-field type-temperature dependence with a critical exponent of $\beta = 0.5$ [9]. In order to describe the step-like behaviour of the elastic constants the lowest-order strain–order parameter coupling term in the Landau free energy is of the form $g\eta^2\epsilon_s$ i.e. the strain is a secondary order parameter [15]. In order to incorporate the temperature hysteresis of the elastic constants, the free energy expansion as a function of the order parameter would have to be at least of sixth order.

We will briefly discuss two Landau free-energy expansions given in the literature [6, 7] which approach the description of the various phase transitions very differently. Falk [6] focuses on the first-order martensitic phase transition taking the shear strain ϵ_s as the primary order parameter. The resulting temperature dependence of the transverse elastic constant $(c_{11} - c_{12})/2$ exhibits qualitatively the experimentally observed features, characterized by a positive temperature coefficient in the β-phase and a sharp increase of $(c_{11}-c_{12})/2$ upon cooling in the martensitic phase. We did not find the calculated linear temperature dependence of $(c_{11} - c_{12})/2$ in the β-phase above A_f (see figure 1(b)) because the strain is only a secondary order parameter as pointed out earlier.

While the *ansatz* of [6] does not take into account the occurrence of the premartensitic phase transitions, Folkins *et al* [7] have presented a Landau model exclusively for these intermediary phase transitions taking a soft-mode order parameter associated with an incommensurate q in the vicinity of $q_1 = \frac{1}{3}\langle 110\rangle 2\pi/a$. In this case the strains are secondary order parameters. This model was designed for observations on the ternary alloy $Ni_{47}Ti_{50}Fe_3$ where the initial pre-martensitic SL phase is an incommensurate phase [16] as observed also in NiTi [13, 17]. Since sound waves probe properties of the crystal corresponding to $q \simeq 0$ wavevectors, we cannot distinguish between incommensurability and commensurability of the order parameter. The complex analysis in [7] is not extended to include the effects of sixth-order terms of the order parameter on the elastic constants. However, it was shown that, depending on which components of the six-component order parameter become non-zero, a rhombohedral lattice distortion is induced and a lock-in transition to the commensurate R-phase at R_s may occur. Furthermore the strain–order parameter coupling term of the type $g\eta^2\epsilon$ for the shear strains ϵ_{yz}, ϵ_{xz} and ϵ_{xy} yields the result that a decreasing elastic constant c_{44} corresponds to an increasing rhombohedral distortion in the R-phase [7, 15].

Our data strongly suggest a coupling of the order parameter to the shear strains being secondary order parameters. This is indicated by the pronounced step-like behaviour of c_{44} and the superimposed minimum at R_s = 310 K upon cooling in comparison with the heating cycle with the R-phase does not appear (see figure 1(c)). The anomaly of the longitudinal mode $(c_{11} + c_{12} + 2c_{44})/2$ seems to be dominated by the contribution of c_{44}. The pre-martensitic soft-mode induced SL phase at S_s = 320 K and the martensitic phase transition at M_s = 300 K couple strongly to $(c_{11} - c_{12})/2$. Figure 1 shows that all modes, but particularly the transverse modes $(c_{11} - c_{12})/2$ and c_{44}, already exhibit softening above the phase transitions. This can be described by taking into account the presence of order parameter fluctuations. The temperature dependence of the elastic constants then takes the form $c(T) = c_0 - aT/(T - T_0)^\rho$ where c_0 is the background elastic constant and ρ is a critical parameter [15]. A complete description of the behaviour of the elastic constants has to await a thorough theoretical analysis at least in the framework of the Landau theory.

A comparison between our absolute values of all elastic constants with those obtained by other groups is presented in table 1. The neutron scattering results [13] which were measured on the same sample compare well with our results except for the longitudinal mode $(c_{11} + c_{12} + 2c_{44})/2$. The comparison with the other groups has to be done cautiously because of different stoichiometry and sample quality. The temperature dependence of the elastic constants measured by Mercier *et al* [13] show only very weak anomalies compared with our measurements which could be related to sample quality. Khachin *et al* [4] give no figures concerning the accuracy of their data.

Table 1. Elastic constants of NiTi in GPa.

	This work	[3]	[4]	[13]
Temperature [K]	400	300	400	400
Composition	$Ni_{50.5}Ti_{49.5}$	$Ni_{55}Ti_{45}$	$Ni_{51}Ti_{49}$	$Ni_{50.5}Ti_{49.5}$
$(c_{11}+c_{12}+2c_{44})/2$	154	183	—	190[a]
$(c_{11}-c_{12})/2$	17	17	18	19
c_{44}	34	35	38	38

[a] M Müllner, unpublished.

Acknowledgments

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References

[1] Wang F E, DeSavage B F, Buehler W J and Hosler W R 1968 *J. Appl. Phys.* **39** 2166
[2] Shabalovskaja S A 1985 *Phys. Status Solidi* b **132** 327
[3] Mercier O, Melton K N, Gremaud G and Hägi J 1980 *J. Appl. Phys.* **51** 1833
[4] Khachin V N, Muslov S A, Pushin V G and Chumlyakov Yu I 1987 *Sov. Phys. Dokl.* **32** 606
[5] Bradley D 1965 *J. Acoust. Soc. Am* **37** 700
Pace N G and Saunders G A 1970 *Phil. Mag.* **22** 73
[6] Falk F 1980 *Acta Metall.* **28** 1773
[7] Folkins I and Walker M B 1989 *Phys. Rev.* B **40** 255
[8] Bührer W, Gotthardt R, Kulik A, Mercier O and Staub F 1983 *J. Phys. F: Met. Phys.* **13** L77
[9] Tietze H, Müllner M, Selgert P and Assmus W 1985 *J. Phys. F: Met. Phys.* **15** 263
[10] Herget G, Müllner M, Suck J B, Schmidt R and Wipf H 1989 *Europhys. Lett.* **10** 49
[11] Hansen M and Anderko K 1958 *Constitution of Binary Alloys* 2nd edn (New York: McGraw-Hill)
[12] Weber D *et al* to be published
[13] Herget G 1990 *PhD Thesis* Johann Wolfgang Goethe-Universität Frankfurt
[14] Zener C 1947 *Phys. Rev.* **71** 846
[15] Brill T M, Hampel G, Mertens F, Schürmann R, Assmus W and Lüthi B 1991 *Phys. Rev.* B **43** 10548
[16] Shapiro S M, Noda Y, Fujii Y and Yamada Y 1984 *Phys. Rev.* B **30** 4314
[17] Pushin V G, Khachin V N, Savvinov A S and Kondrat'ev V V 1984 *Sov. Phys. Dokl.* **29** 681