

On the proposed martensitic-like structural transformation in V, Nb, and Ta

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The transition metals Nb, Ta and V have been known to be cubic at all temperatures, until recently the existence of a martensitic transformation has been reported, based on anomalies in the thermal expansion at low temperatures. Such a structural transformation would have passed unnoticed, because it would be hindered by small amounts of impurities. This finding is discussed in the light of anelastic measurements on Nb samples whose purities are comparable to those presenting the dilatometric anomalies. It results that the effects of the alleged transformation on the anelastic spectra would be at least three orders of magnitude smaller than in typical martensitic transformations. A possible alternative explanation for the observed anomalies is proposed in terms of precipitation of unnoticed residual H.

Keywords: martensite transformations, acoustic spectroscopy, thermal expansion, transition metals, low temperature.

1. Introduction

In an intriguing Letter [1] it has been reported that crystals of pure Nb, Ta and V exhibit a splitting of the thermal expansion along the $\langle 100 \rangle$ directions below room temperature, attributed to a previously unknown martensitic transformation (MT). The occurrence of the MT would be prevented by impurities at levels as low as few hundreds at ppm, so explaining why it had never been noticed before [1]. It is even postulated that the structural instability in A-15 intermetallics like Nb₃Sn is due to the presence of the Group-Va element itself [1], rather than to their correlation in one-dimensional chains, as usually accepted [2]. This is a provocative finding, since Nb, Ta and V have been thoroughly studied for decades starting from the 1960s, and are known to have bcc structure at all temperatures. In order to induce a structural instability in V, a pressure of 69 GPa must be applied, so causing a rhombohedral distortion of the cell [3], while Nb exhibits some shallow softening of the c_{44} elastic constant above room temperature [4], and Ta presents the same effect at ~ 80 GPa [5], but neither Nb nor Ta have been found to complete the transition to the rhombohedral state.

Many investigations on these group Va transition metals have been conducted by various experimental techniques, including anelastic relaxation and neutron scattering, which are also the most sensitive techniques in detecting martensitic transformations. Those investigations

were not focused on martensitic transformations, but on dislocations and their interaction with the gaseous impurities H, O, N and C [6–8], or the absorption, diffusion, trapping and tunneling of such impurities, particularly H, and the complex $x-T$ phase diagrams of MH_x (M = V, Nb, Ta) [9–11], or the coupling of the superconducting transition to the lattice [12]. These studies were made on variously doped samples, but in some cases with quite low levels of impurities [13,14] or undoped [13]. Considering the sensitivity of the anelastic measurements to structural phase transitions, a traditional martensitic transformation would hardly have passed unnoticed.

Also the electronic structure of these transition metals has been thoroughly studied both experimentally and theoretically and has been shown to be at the origin of the tendency or manifestation of structural instability at high temperature and pressure. The softening of the shear elastic constant c_{44} is driven by a combination of intraband nesting of the Fermi surface, electronic topological transition, and band Jahn–Teller effect [5,15]. When the softening becomes complete, as in V at high pressure, the lattice becomes unstable against shears of the ϵ_4 type (Voigt notation) and becomes rhombohedral, but in Nb and especially Ta this instability is more than counterbalanced by the Madelung contribution to the elastic energy [5,15,16]. Tantalum is even considered as “prototype metal for the investigation and calibration of equation of state and material strength at extreme thermodynamics conditions” [5].

For these reasons, a report of martensitic-like transformations so far unnoticed in V, Nb and Ta should be carefully considered and verified also by the methods most sensitive in detecting MTs. Experimental techniques widely used to study the MTs are diffraction experiments, revealing splittings of the Bragg peaks, TEM revealing the twin domains of the low-symmetry phase, and anelastic or ultrasonic experiments exhibiting cusped or step-like softening of the shear moduli involved in the transformation and elastic energy loss from the movement of the twin boundaries. None of these features has ever been reported in pure and dislocation-free V, Nb and Ta. Yet, the lack of evidence of MT from the existing studies might be due to the fact they were mostly made on samples with contents of impurities, either added or unwanted or unknown, that would hinder the transformation. Indeed, anelastic relaxation experiments have been done also on crystals much purer than those of Ref. 1, for example, on a Nb crystal with residual resistivity ratio $RRR = 10000$ measured with the composite oscillator technique [6], or a Ta crystal with $RRR = 17000$ measured with the torsion pendulum [17], which did not show signs of phase transformations. These experiments, however, were devoted to studying dislocations on deformed samples, so that the reported anelastic spectra are dominated by the motions of dislocations. The search for a MT hindered by minimal amounts of impurities was not an issue and to my knowledge there are no reports of the background complex elastic moduli of undeformed samples with very high purity. Since the level of impurities seems to be critical in revealing the MT, here are presented the anelastic spectra of two samples of Nb with purities as close as possible to those where a MT appears in Ref. 1.

2. Experimental

Sample #1 was a $50 \times 5 \times 0.67$ mm polycrystalline bar prepared by Prof. G. Hörz (MPI für Metallforschung, Inst. für Werkstoffwissenschaften, Stuttgart). The residual resistivity ratio was $RRR = R(296 \text{ K})/R(0 \text{ K}) = 320$, very close to the value of 347 of the pure Nb crystal of Ref. 1, from which a residual resistivity $\rho(0 \text{ K}) = 6.13 \cdot 10^{-2} \mu\Omega\text{-cm}$ is deduced. Assuming that the main contribution is from interstitial O, which contributes with $4.5 \cdot 10^{-10} \Omega\text{-cm/at ppm O}$ [18], the impurity content was $c_{\text{O}} \lesssim 136$ at. ppm, the < sign being due to the fact that the anelastic spectrum showed also the presence of H. Sample #2 was a $40 \times 4.5 \times 0.56$ mm bar cut from Marz grade polycrystalline Nb, previously subjected to various thermal treatments during which O uptake occurred. The O content estimated from $RRR = 26.5$ was $c_{\text{O}} = 1200$ ppm, about ten times larger than in sample #1, but close to that of the pure Ta crystal of Ref. 1. The impurity content of sample #2 might also be higher than those of the heat treated samples of Ref. 1, which are not specified. The dynamic Young's modulus $E(\omega, T) = E' - iE''$ was

measured by suspending the samples on thin thermocouple wires and electrostatically exciting the flexural modes [19]; the first and fifth flexural modes, whose nodal lines practically coincide and whose frequencies are in the ratio 1:13.3, could be measured during a same run.

3. Results and discussion

Figure 1 presents the anelastic spectra of the above samples: the upper panel contains the relative change of E' with respect to its 0 K value, and the lower panel contains the elastic energy loss coefficient $Q^{-1} = E''/E'$. Of sample #1 are shown the $Q^{-1}(T)$ curves measured at both 1 and 13 kHz (closed symbols). The almost linear rise of $Q^{-1}(T)$ is thermoelastic effect [20,21], namely the diffusion of heat between the alternately expanded and compressed faces of the bar during the flexural vibration, with consequent out-of-phase expansion of the heated region. In sample #2 (open symbols) there is no trace of additional dissipation mechanisms, while in sample #1 (closed symbols) there are two peaks at ~ 90 K and ~ 190 K. These peaks are shifted to higher T when measured at higher frequency (smaller symbols) and therefore are due to thermally activated relaxations. The peak at ~ 90 K is readily recognized from its temperature and activation energy as due to the hopping of residual H trapped by O [22,23], while the peak at ~ 190 K is associated with the simultaneous presence of H and dislocations [8,24]. It turns out that,

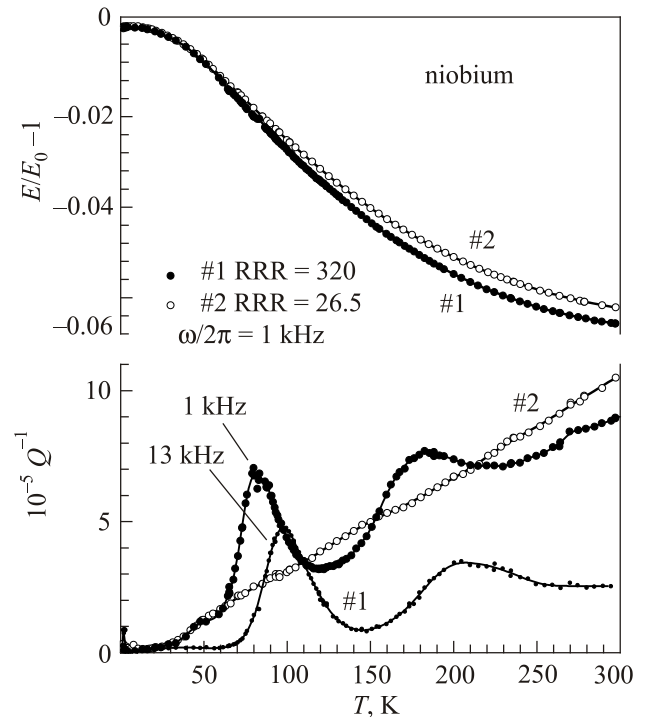


Fig. 1. Relative change of the Young's modulus E and elastic energy loss coefficient $Q^{-1} = E''/E'$ measured on two samples of Nb with different purities.

in spite of the fact that sample #1 has a RRR 12 times higher than that of sample #2, its content of residual H and dislocations is larger. The seeming inconsistency is due to the fact that H contributes little to the residual resistivity, especially when it is trapped by an impurity like O, and dislocations contribute even less. Therefore, the RRR provides a good estimate of the content of heavy gaseous impurities, but neither of H nor of dislocations. The ~ 130 at. ppm O impurities can trap about as many H atoms, and if untrapped H in excess is also present, it would partially precipitate into β phase hydride. When this precipitation from the gas-like α phase to the $\alpha + \beta$ phase occurs, it is accompanied by the formation of dislocations at the phase interfaces and manifests itself in the anelastic spectrum as a sharp rise of dissipation and anomalies in the modulus [9,10,25,26]. The absence of a clear precipitation peak indicates that, if any additional H was present in solid solution, its precipitation might have only occurred below 150 K, and therefore could not exceed hundred at. ppm. One or two hundred at. ppm is the typical residual content of H even after prolonged outgassing treatments in UHV, unless particular precautions are taken, like applying a film of Pd on the sample surface [17], or an oxide layer during cooling from the high-temperature annealing [27].

The real parts of the modulus do not present any anomaly attributable to structural instabilities, except for the well known shallow softening above room temperature from the Fermi surface topology and electron-phonon coupling, which appears as a positive curvature of the $E(T)$ curve. There is a drop of $E(T)$ below the superconducting transition at 9.2 K [12], again due to the electron-phonon coupling, but is invisible on the scale of Fig. 1.

The curves in Fig. 1 exclude the occurrence of any structural transformation near or below room temperature with a sensitivity much higher than diffraction experiments. In fact, a MT would appear as a step-like or cusped softening [28] with amplitudes up to several tens of percent in the polycrystalline Young's modulus E [29], which contains all the elastic constants, but no trace of it is found in Fig. 1. In addition, the motion of the twin walls formed in the low-symmetry phase would cause a very broad thermally activated maximum with sharp onset at the transformation, whose typical amplitude is [28,29] $\Delta Q^{-1} = 10^{-3} - 10^{-1}$. A similar anomaly, if present in Fig. 1, cannot have an amplitude above few 10^{-6} . It can be concluded that, if a MT occurs in any of the two samples, it causes elastic and anelastic anomalies with an amplitude at least three orders of magnitude smaller than in the known cases of MTs.

It should be stressed that a transformation where the order parameter is strain (ferroelastic transformation), is best detected in the complex elastic modulus (or its reciprocal, the compliance), exactly as a ferroelectric or magnetic transition appears in the dielectric and magnetic susceptibilities. Therefore, in the absence of a clear splitting of the

Bragg peaks in diffraction experiments, the hard evidence for a ferroelastic transformation should come from elastic and/or anelastic anomalies, just like the case of the ferroelectric and ferromagnetic transitions, where the main evidence is the Curie–Weiss peak in the respective susceptibility. This is true also if strain is not the primary order parameter, but only coupled to it, so causing a possibly small step-like anomaly in the compliance, rather than a Curie–Weiss peak [30]. In fact, whatever the nature of the transition, if the cell departs from the cubic shape, it will lead to the formation of domain walls, whose motion enhances the mechanical loss to levels much higher than the $Q^{-1}(T)$ curves in Fig. 1.

These data show that the absence assumed so far of structural transformations near and below room temperature in Nb is not due to a high amount of impurities, since it persists at the same content of impurities as in Ref. 1. In addition, the anelastic spectrum is much more sensitive and selective in characterizing the status of the sample than resistivity, which is little sensitive to H and even less to dislocations. It can be concluded that the interpretation of the thermal expansion anomaly in Nb, Ta and V as due to a MT [1] is problematic. Lacking an anelastic characterization of those samples, an alternative explanation can only be speculated in terms of unwanted interstitial H and dislocations. In fact, the estimate in Ref. 1 of < 0.05 at.% H from the Vickers hardness H_V and lattice parameters [31] seems unreliable, since the error bars and dispersion of points in the plot of H_V vs x in Fig. 5 of Ref. 31 (setting $c_H \equiv x$ in NbH_x) do not allow estimates better than $\Delta x \sim 0.005$. This estimate may still seem to exclude that the precipitation of H is at the origin of the anomalies with onset just below room temperature, since the solvus line $x(T)$ separating α and $\alpha + \beta$ phases in NbH_x is close to 0.03 at room temperature. Yet, the reported solvus line is not a true border at thermodynamic equilibrium, but presents large hysteresis between heating and cooling and can be shifted to higher temperature of tens of kelvins just by repeating the temperature cycles [10,32]. This is due to the fact that once the precipitates of β phase are plastically accommodated, the plastic deformation remains and allows subsequent precipitations to occur at higher temperature. As a consequence, the anomalies found in Nb [1] are not incompatible with precipitation of H with $x \sim 0.01$, if they are measured after the first cooling run. This is especially true for the anomalies in V and Ta, which appear well below room temperature and might be accounted for by a much lower content of H.

Another issue in the interpretation of the anomalies in the thermal expansion in terms of MT [1] is their anisotropy on a macroscopic scale. It is unlikely that, in crystals with edges long up to 3.5 cm, the transformation strains of the twin domains do not average in all directions and instead the edges present different elongations, unless the crystals are strained or rich in dislocations. Analogously,

ferromagnetic or ferroelectric materials do not acquire macroscopic magnetization or polarization in the absence of an external field or anisotropic defects.

4. Conclusion

In conclusion, a convincing evidence of the existence of a martensitic-like transformation in Nb, Ta and V can come from anelastic or diffraction experiments, but the existing anelastic measurements, including those presented here, provide a negative answer so far.

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Про уявне мартенситоподібне структурне перетворення у V, Nb та Ta

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До недавнього часу вважалося, що перехідні метали Nb, Ta та V залишаються кубічними при всіх температурах, аж поки не з'явилося повідомлення про існування в них мартенситних перетворень. Повідомлення, яке базувалося на аномаліях, що спостерігалися при вивченні теплового розширення при низьких температурах. Стверджувалося, що це структурне перетворення залишалось непоміченим лише тому, що його прояву заважала невелика кількість домішок. Цей висновок обговорюється з урахуванням вимірювань непружності, проведених на зразках Nb, чистота яких порівнянна з тими, на яких були виявлені дилатометричні аномалії. В результаті встановлено, що вплив перетворення, що було припущене, на непружні спектри є як мінімум на три порядки меншим, ніж у типових мартенситних перетвореннях. Пропонується можливе альтернативне пояснення спостережених аномалій у термінах утворення преципітатів з непоміченого залишкового H.

Ключові слова: мартенситні перетворення, акустична спектроскопія, теплове розширення, перехідні метали, низькі температури.

О предполагаемом мартенситоподобном структурном преобразовании в V, Nb и Ta

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До недавнего времени считалось, что переходные металлы Nb, Ta и V остаются кубическими при всех температурах, пока не появилось сообщение о существовании в них мартенситных

превращений. Сообщение основывалось на аномалиях, которые наблюдались при изучении теплового расширения при низких температурах. Утверждалось, что данное структурное преобразование оставалось незамеченным лишь потому, что его проявлению мешало наличие небольшого количества примесей. В настоящей работе сделанный вывод обсуждается с учетом измерений неупругости на образцах Nb, чистота которых сравнима с теми, на которых выявлены дилатометрические аномалии. В результате установлено, что влияние предполагаемого превращения на спектры неупругости как

минимум на три порядка меньше, чем в обычных мартенситных превращениях. Предлагается возможное альтернативное объяснение зарегистрированных аномалий в терминах образования преципитатов из неучтенного остаточного H.

Ключевые слова: мартенситные превращения, акустическая спектроскопия, тепловое расширение, переходные металлы, низкие температуры.