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

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A recent announcement, after anomalies in the thermal expansion, of a previously unknown martensitic transformation in pure Nb, Ta and V is discussed in the light of anelastic measurements on Nb samples with comparable purities. 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.

I. INTRODUCTION

In an intriguing Letter\textsuperscript{1} it has been reported that crystals of pure Nb, Ta and V exhibit a splitting of the thermal expansion along the (100) 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\textsuperscript{2}. It is even postulated that the structural instability in A-15 intermetallics like Nb\textsubscript{3}Sn is due to the presence of the Group-Va element itself\textsuperscript{2}, rather than to their correlation in one-dimensional chains, as usually accepted\textsuperscript{3}. 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\textsuperscript{4}, while Nb exhibits some shallow softening of the $c_{44}$ elastic constant above room temperature\textsuperscript{4}, and Ta presents the same effect at $\sim 80$ GPa\textsuperscript{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 aimed at studying dislocations and their interaction with the gaseous impurities H, O, N and C, while object of other investigations were the absorption, diffusion and trapping of such impurities, particularly H, and the complex $x-T$ phase diagrams of MH$_2$ (M = V, Nb, Ta)\textsuperscript{6,7}. Many of these investigations have been conducted by anelastic relaxation and neutron scattering, which are also the most sensitive in detecting martensitic transformations, but none had been detected so far.

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\textsuperscript{5,9}. When the softening becomes complete, as in V at high pressure, the lattice becomes unstable against shears of the $\varepsilon_4$ 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\textsuperscript{5,9,10}. Tantalum is even considered as "prototype metal for the investigation and calibration of equation of state and material strength at extreme thermodynamics conditions"\textsuperscript{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 steplike softening of the shear moduli involved in the transformation and elastic energy loss from the movement of the twin boundaries. None of these features have 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\textsuperscript{5}, for example on a Ta crystal with residual resistivity ratio $\text{RRR} = 17000$ measured with the torsion pendulum\textsuperscript{11}, and did not show hints to 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\textsuperscript{1}.

II. EXPERIMENTAL

Sample #1 was a $50 \times 5 \times 0.67$ mm$^3$ polycrystalline bar prepared by Prof. G. Hörz (MPI für Metallforschung, Inst. für Werkstoffwissenschaften, Stuttgart). The residual resistivity ratio was $\text{RRR} = R(296 \text{ K})/R(0 \text{ K}) =$
320, very close to the value of 347 of the pure Nb crystal of Ref.14, from which a residual resistivity $\rho(0\ K) = 6.13 \times 10^{-2}\ \mu\Omega\mathrm{cm}$ is deduced. Assuming that the main contribution is from interstitial O, which contributes with $4.5 \times 10^{-10}\ \Omega\mathrm{cm}/\mathrm{at}\ ppm\ O_{12}$, the impurity content was $c_O \lesssim 136$ at ppm, the < sign being due to the fact that the anelastic spectrum showed also the presence of H. Sample #2 was a $40 \times 4.5 \times 0.56\ mm^3$ 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 $c_O \approx 1200$ ppm, about ten times larger than in sample #1, but close to that of the pure Ta crystal of Ref.13.

Sample #2 was a 40 µm thick Nb foil. In the upper panel of Fig. 1 presents the anelastic spectra of the above samples: the upper panel contains the relative change of the dynamic Young’s modulus $E(\omega, T) = E' - iE''$ measured on two samples of Nb with different purities.

III. 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 effects14,15, 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 $\sim 90$ K and $\sim 190$ 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 $\sim 90$ K is readily recognized from its temperature and activation energy as due to the hopping of residual H trapped by O16,17, while the peak at $\sim 190$ K is associated with the simultaneous presence of H and dislocations18,19. It turns out that, 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 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, 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 steplike or cusped softening22 with amplitudes up to several tens of percent in the polycrystalline Young’s modulus $E$.
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 on-
set at the transformation, whose typical amplitude is
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from the cubic shape, it will lead to the formation of do-
whatever the nature of the transition, if the cell departs
compliance, rather than a Curie-Weiss peak
it, so causing a possibly small step-like anomaly in the
is not the primary order parameter, but only coupled to
in the respective susceptibility. This is true also if strain
is best detected in the complex elastic modulus (or its
order parameter is strain (ferroelastic transformation),
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 mag-
netic 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 transi-
tions, 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. In fact,
whatever the nature of the transition, if the cell departs
from the cubic shape, it will lead to the formation of do-
main 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 tempera-
ture 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 is problematic. Lacking an
anelastic characterization of those samples, an alterna-
tive explanation can only be speculated in terms of un-
wanted interstitial H and dislocations. In fact, the esti-
mate in Ref. 1 of $<0.05$ at\% H from the Vickers hardness
$H_V$ and lattice parameter seems unreliable, since the
error bars and dispersion of points in the plot of $H_V$ vs
$x$ in Fig. 5 of Ref. 20 (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 $\alpha$ and
$\alpha + \beta$ phases in NbH$_x$ is close to 0.03 at room tempera-
ment. Yet, the reported solvus line is not a true border at
thermodynamic equilibrium, but presents large hysteres-
sis between heating and cooling and can be shifted to
higher temperature of tens of kelvins just by repeating
the temperature cycles. This is due to the fact that
once the precipitates of $\beta$ phase are plastically accommod-
ated, the plastic deformation remains and allows subse-
quent precipitations to occur at higher temperature. As
a consequence, the anomalies found in Nb are not in-
compatible with precipitation of H with $x \sim 0.01$, if they
are measured after the first cooling run. This is especially
ture 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 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.

IV. 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 pre-
sented here, provide a negative answer so far.

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