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Observation of a Martensitic Structural Distortion in the Elements V, Nb, and Ta

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Thermal-expansion measurements of the Group 5 elements V, Nb, and Ta reveal a structural distortion below 300 K. Data for single-crystalline Nb and Ta, display anisotropic thermal expansion, martensitic in character, that is inconsistent with cubic crystal structures at low temperature. Published results on V show similar behavior. Interstitial impurities suppress the transition.

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Cubic elements can exhibit structural distortions that are typically accompanied by a softening of the shear elastic modulus and phonon modes [1]. Examples include the Group 3 and 4 elements [2], Na [3], Li [4], and Yb [5], which are body-centered cubic at high temperature [6] with rhombohedral (Na) [3] or hexagonal (Sc, Y, La, Li, and Yb) low-temperature structures [2, 4, 5]. These structural distortions are generally called *martensitic phase transitions*. They are first order, displacive in nature, generally associated with distortions from body-centered cubic to a close-packed structure, and the low-symmetry phase occurs at low temperature [7]. In some cases, the transformation is incomplete at the lowest temperature measured [3]. The presence of small impurity concentrations can suppress these transitions [5].

This letter reports high-resolution thermal-expansion measurements of the elements V, Nb, and Ta. The latter two are believed to be bcc from $T = 0$ K to the melting point, but our measurements reveal a structural distortion on cooling below 300 K. Similar behavior is known for V, where two low-temperature phases, body-centered tetragonal [8] and body-centered orthorhombic, [9] have been proposed. In all three cases, the character of the transition associated with the distortion is broad and hysteretic. This behavior is reminiscent of martensitic phase transitions. The results impact our general knowledge of these elements, and have implications for anisotropy observed in their superconducting states [10], and for a similar structural transition in the well-known A15 superconductors [11–13].

Single-crystalline Nb (1 cm diameter, 3.5 cm long) and Ta (4x5x9 mm^3) were prepared via electron-beam melting, followed by an acid etch to remove surface damage, and an anneal in a Ta boat (7 hours at 2320 K in a dynamic vacuum of $\sim 1\times10^{-5}$ mbar), from which the crystals were quenched (in < 5 min) to room temperature to minimize the uptake of interstitial gases [14]. The Nb crystal conforms to the ASTM-B-391 standard; analysis of similarly-prepared crystals reveals 100-200 wt. ppm of dissolved gases (O, C, N, and H). The residual resistivity ratios ($R_{296\,\mathrm{K}}/R_{4.2\,\mathrm{K}}$) are 347 and 29 for Nb and Ta, respectively. Polycrystalline V (99.5%), Nb (99.99%), and Ta (99.98%) were obtained from Alfa Aesar [15]. Samples termed *heat treated* were placed in quartz tubes containing Zr foil, which were flushed with dry He gas, evacuated to $\sim 10^{-6}$ mbar, sealed, heated to 1300 K for ten hours, and cooled at 0.5 K/min to 296 K. This type of treatment is well known to introduce interstitial oxygen via diffusion of the surface oxide layer [16, 17]; no mass change of the heat treated samples was detected within our resolution (0.1%). Thermal-expansion measurements utilized a fused-quartz dilatometer [19], which exerts a maximum uniaxial force of 400 mN (equivalent to a pressure of 0.04 MPa). Electrical resistivity and specific heat were measured using a four-wire technique and thermal relaxation, respectively. Single crystals were oriented using Laue diffraction. Vicker's hardness of the Nb crystals was measured with a LECO LM100AT; the obtained value (49(2)VH0.200) is consistent with an upper limit of 0.05 at.% hydrogen [20].

The linear thermal expansion $\Delta L/L_{296\,\mathrm{K}} = (L(T) - L_{296\,\mathrm{K}})/L_{296\,\mathrm{K}}$ was measured along the three orthogonal <100> directions (relative to cubic structure) of the Nb single crystal. The $\Delta L/L_{296\,\mathrm{K}}$ data clearly show a structural distortion beginning below 296 K that results in distinct differences at 5 K for each direction, with one direction's $\Delta L/L_{296\,\mathrm{K}}$ larger than the other two (which are comparable). Our observations reveal that Nb's thermal expansion is anisotropic over a broad temperature range, and therefore inconsistent with cubic symmetry. As part of this investigation, two additional, similarly-prepared, Nb single crystals were measured; they corroborate these results. Surprisingly, one of the three <100> directions elongates relative to the other two on cooling and subsequent measurements reveal the same direction to elongate. This may be the result of dislocation formation during the first cooling, that gives a preferred orientation to the low-temperature phase.

The coefficient of linear thermal expansion, $\alpha = \mathrm{d}(\Delta L/L_{296\,\mathrm{K}})/\mathrm{d}T$, is shown in Fig. 1(b). These data reveal two notable aspects of the transition: (1) it is very broad, existing in the region 140 K $< T <$ 300 K and (2)

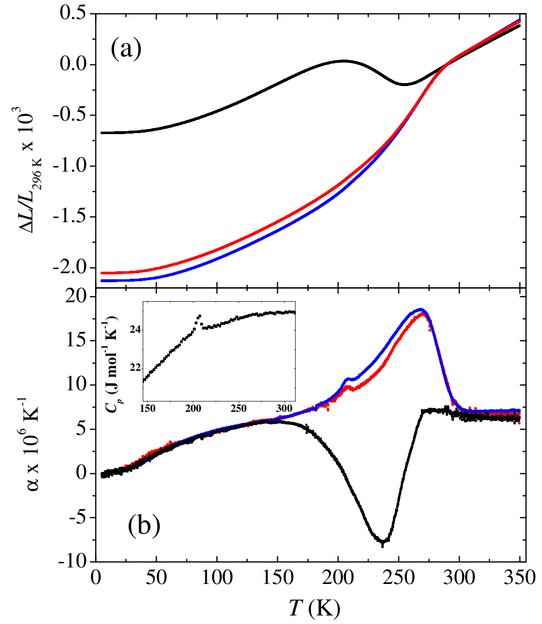

FIG. 1: (color online) (a) Linear thermal expansion for single crystal Nb measured along the three cubic <100> directions, (b) coefficient of thermal expansion. Over 1700 data points appear in each curve. Inset shows specific heat versus temperature.

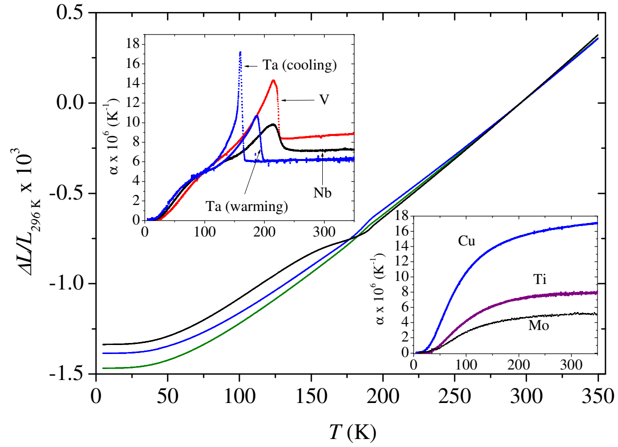

FIG. 2: (color online) $\Delta L/L_{296\,\mathrm{K}}$ for single crystal Ta, measured along the three cubic <100> directions. Upper inset shows α for polycrystalline V, Nb and Ta; hysteresis in Ta is evident. Lower inset shows our α for polycrystalline Cu, Ti, and Mo.

above and below the transition α is nearly identical for all three directions. There is little evidence of the transition in the specific heat C_p (inset of Fig. 1(b)), with only a small peak at 208 K that is coincident in T to features in α along the two $\alpha > 0$ directions measured. However, it is plausible that a very broad feature of small magnitude is present in the C_p data [21].

In the main panel of Fig. 2, $\Delta L/L_{296\,\mathrm{K}}$ for single crystalline Ta is shown. The transition begins when cooled below 190 K and the distortion that is realized by 5 K is far smaller than that observed in Nb, although the purity of this crystal, based on the $R_{296\,\mathrm{K}}/R_{4.2\,\mathrm{K}}$ values, is lower than that of the Nb crystal. The upper inset shows α for polycrystalline samples of V, Nb, and Ta; all three exhibit a transition. Cooling and warming data for Ta reveal significant hysteresis. The lower inset shows our $\alpha(T)$ data for Cu, Ti, and Mo illustrating that the transition does not appear in the cubic Group 6 and 11 elements Mo and Cu. Ti is hexagonal, having transformed from cubic well above our temperature range. Note that the polycrystal data represent one third of the volumetric thermal expansion coefficient, neglecting possible effects of preferred orientation.

Insight regarding the phase transition's nature can be gleaned from Fig. 3. The main panel shows α for one orientation of our single-crystal Nb sample after cooling at 0.2 K/min, 1.0 K/min, and our fastest possible rate (10 - 12 K/min). Cooling was controlled from 350 K to 77 K, which encompasses the temperature range of the transition. The data were acquired on warming at 0.200 K/min. The largest peak corresponds to the lowest cooling rate. Good agreement between the curves is observed above 300 K and below 140 K, but the transition region is influenced by the cooling rate. The fact that the magnitude of the peak *decreases* with an *increased* rate suggests that rapid cooling inhibits nucleation of the low-temperature phase, or leads to small, disordered domains of that phase. Presumably, cooling at rates $\ll$ 0.2 K/min would sharpen the peak. The inset of Fig. 3 shows α along another direction measured on cooling and warming (both at 0.2 K/min). Significant hysteresis indicates that the transition is first order. The presence of a broad, hysteretic anomaly in α observed in Nb, Ta (inset of Fig. 2), and V [8, 9], reveals that these Group 5 metals undergo a structural distortion of similar nature, that appears to be martensitic in character.

Heat-treated (HT) V, Nb, and Ta do not exhibit the phase transition in α (Fig. 4(a)). In the case of the Nb single crystal, $\rho(T)$ measurements were made to estimate impurity concentrations [14]. The residual resistivity ratio decreased from 347 to 66 after the heat treatment, with a substantial increase in the residual resistance (upper inset of Fig. 4(b)). Based on the residual resistance magnitudes at 4.27 K (4.62 x 10^{-10} Ωm and 2.20 x 10^{-9} Ωm for the virgin and HT samples, respectively), the impurity concentration was estimated to have increased by ~386 ppm impurity-atoms/Nb [14]. This is a result of the surface-oxide layer, always present on Group 5 elements when exposed to air, dissolving into the sample during the heat treatment [16–18]. Along with the increase of oxygen defects, the heat treatment relieves strain associated with the anisotropic expansion of the virgin sample, strain from quenching after the high temperature anneal, and strain from cutting the sample. Strain results in a

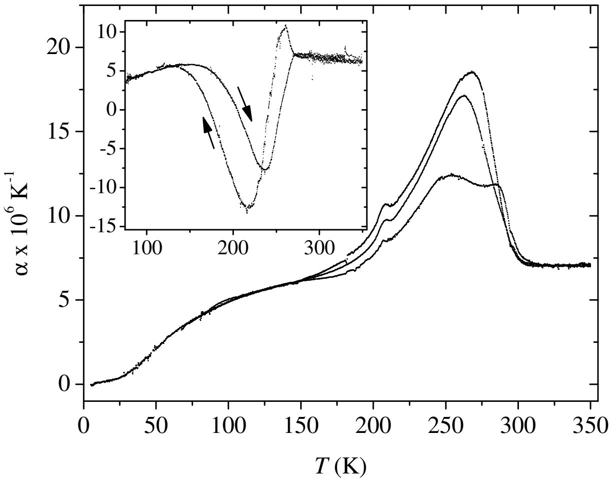

FIG. 3: α along a single [100] direction for single crystal Nb using three cooling rates (top to bottom: 0.2 K/min, 1.0 K/min and 10 - 12 K/min). Inset shows hysteresis for another orientation.

higher superconducting transition temperature T_c, and a broader transition [22], as seen in the virgin Nb sample (Fig. 4(b) inset, solid squares). Interstitial O suppresses T_c in Nb by 0.93 K/at.% [23]. Thus, we believe that the combined effects of strain relief and interstitial oxygen are responsible for the decrease in T_c (from 9.35 K to 9.25 K). V and Ta also absorb impurities during heat treatments such as those used here [24, 25]. Our results show that the introduction of interstitial impurities beyond a certain limit, in the 100 ppm impurity-atoms/host-atom range, is enough to completely suppress the martensitic phase transition in V, Nb, and Ta.

Two strain experiments were conducted: (1) the virgin Nb single crystal was irreversibly strained by ~30%, which did not affect the martensitic transition and (2) similar strain on the HT sample did not cause the transition in $\rho(T)$ to reappear. We thus conclude that global strain via deformation does not play a significant role and strain relief due to the heat treatment cannot explain the transition's absence. Strain increased the residual resistance (by 45% and 14%, respectively) indicating its role in increasing the defect density of the crystals.

Fig. 4(b) shows ρ versus T for the virgin and HT Nb single crystals (with the same random orientation). The virgin sample exhibits a distinct kink in ρ at 250 K on cooling, and 295 K on warming (both at 0.2 K/min), along with significant hysteresis. A similar kink was reported in vanadium [8]. A more subtle kink is also evident near 208 K, coincident to the feature in C_P. To search for relaxation effects, ρ was measured at 285 K for two hours after: (1) heating to 400 K followed by cooling to 285 K and (2) cooling to 50 K followed by warming to 285 K (all done at 20 K/min). ρ remained constant during the 2 hour intervals. The virgin sample also exhibits a significantly higher ρ than the HT sample above the kink in $\rho(T)$ with slope, within the uncertainty, the same as for the HT sample. The higher ρ in the virgin sample suggests that interstitial oxygen affects the phonon frequencies and amplitudes in a manner that reduces electron-phonon scattering.

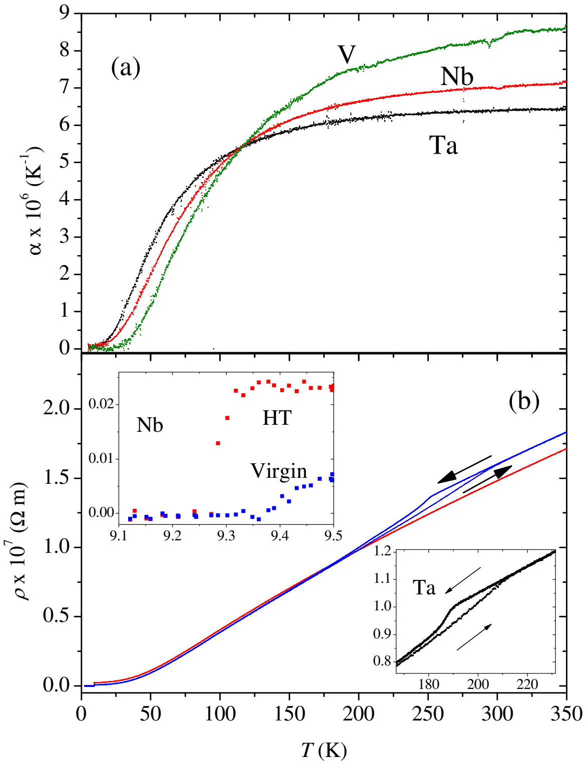

FIG. 4: (a) (color online) $\alpha(T)$ for polycrystalline V, Nb, and Ta after heat treating; no trace of the martensitic transition remains. (b) $\rho(T)$ of single-crystal Nb (random orientation) measured during warming *and* cooling. Virgin sample shows hysteresis, while the HT sample does not. Upper inset shows $\rho(T)$ near T_c; the HT crystal has a larger residual resistivity due to interstitial oxygen. Lower inset shows kink and hysteresis in $\rho(T)$ of the virgin Ta single crystal.

Lattice parameters, determined from measuring the d-spacing between the {200} planes using a x-ray diffractometer with Bragg-Brentano geometry (296 K and Cu K$_{\alpha 1}$ radiation) verified the same d spacing ($2d = 3.3035$ Å) at 296 K for all three directions, within our uncertainty, suggesting that Nb is cubic at 296 K. This experiment was also conducted using higher-resolution x-ray diffraction at the Deutsches Elektronen-Synchrotron (DESY) as a function of temperature down to 60 K [26], yielding the same result. Some broadening and reduction in intensity of the <2 0 0> peak develops with cooling. X-ray diffractometer measurements on polycrystalline Nb exhibit peaks that are too broad (by a factor of 3) to resolve the structural distortion, and are therefore inconclusive. These combined results suggest that the structural distortion is not tetragonal, which might inadvertently be inferred from Fig. 1(a). Extensive diffraction measurements will be required to reveal the subtle crystallographic change associated with this martensitic phase transition.

In prior reports, interstitial hydrogen was blamed for transitions similar to those reported here in ρ [27], C_P [28], and thermal expansion [29] of V. Heat treatment of V (1073 K at 2×10^{-6} mbar [27] and 1000 K at 1×10^{-6} mbar [28]), similar to what was done here, was found to eliminate the transition [27]. In V as well as Nb, diffusion of the surface-oxide layer occurs under these conditions [18]. Our assessment is that interstitial oxygen suppresses the martensitic phase transition that is *intrinsic* to high-purity V, Nb, and Ta, in contradiction to these reports, and that hydrogen contamination does not play a role. Furthermore, our Vickers hardness and lattice parameter measurements are consistent with hydrogen levels of < 0.05 at.% H/Nb [20].

The behavior of the martensitic phase transition in V, Nb, and Ta has a striking resemblance to a well-known structural distortion in the A15 superconductors V_3Si and Nb_3Sn [11–13]. Although the distortion's significance in the A15s was never well understood, it was believed to be important for the unusually high T_c's of these compounds. Similar to our findings, only A15 samples with high residual resistivity ratios exhibit the distortion [13], signifying the destructive role of impurities. We postulate that this distortion may be associated with the presence of the Group 5 element, rather than the A15 compound itself. Another observation is that V, Nb, and Ta are all known to show anisotropy in the superconducting state that was thought to be associated with anisotropy in the Fermi surface [10]. The anisotropy is most commonly observed in the upper critical field, H_{c2}, and occurs in our Nb single crystal as well. We propose that the source of this anisotropy is the crystallographic distortion to lower symmetry revealed herein.

In conclusion, a previously unappreciated martensitic phase transition is *intrinsic* to the Group 5 elements V, Nb, and Ta. This transition results in a crystallographic distortion to lower symmetry below room temperature. Small amounts of interstitial oxygen suppresses the phase transition. The structure of the lower symmetry phase is unknown, as is whether the entire sample transforms, or only a fraction thereof does. Microscopic investigations are required to fully understand the new phase.

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