ANOMALIES IN THE ELASTIC PROPERTIES OF V AND Ta. THE ROLE OF INTERSTITIAL IMPURITIES*

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Anomalies in the elastic constants and thermal expansion of vanadium single crystals in the range 180 to 260 K are reported and discussed in terms of a model of precipitation of hydrogen impurities. An extension of the impurity precipitation model is used to explain the appearance of sharp anomalies in the temperature dependence of the nuclear-acoustic-resonance linewidth in tantalum single crystals.

The existence of anomalies in the temperature dependence of a variety of physical properties of vanadium has been reported previously.[1,2] Although the anomalies have been attributed by different investigators to a variety of physical effects, including the onset of antiferromagnetism, only recently has the work of Westlake[2,3] on vanadium-hydrogen alloys pointed to the role of interstitial hydrogen impurities as an explanation. In this Letter we report the observation of marked anomalies in the elastic constants and thermal expansion of several single crystals of "pure" vanadium, show that the empirical formula developed by Westlake for V-H alloys can be extended to fit our results precisely, and present a physical model to explain the role of interstitial hydrogen in the anomaly in the physical properties of V.

As substantiating evidence for the role of interstitial impurities in the appearance of anomalies in bcc metals we report, in addition, the observation of anomalies in the nuclear-acoustic-resonance (NAR) linewidth in single-crystal tantalum and show that the physical model used to explain the V results can be extended to Ta. To our knowledge, this is the first report of anomalies in the physical properties of "pure" Ta; their appearance in the present investigation testifies to the sensitivity of nuclear acoustic resonance as a probe to investigate static and dynamic effects in metals.

The elastic constants of two crystals of V were measured as a function of temperature. In both crystals marked anomalies were observed in the shear constant $C' \equiv \frac{1}{2}(C_{11}-C_{12})$ and in the compressional constant C_{11}; much smaller effects were observed for C_{44} and $C_l \equiv \frac{1}{2}(C_{11}+C_{12}+2C_{44})$. The data for C' are plotted in Fig. 1; the anomaly in V(I) is seen to occur at 193 K, that in V(III) at 233 K. Although weak anomalies in the thermal expansion were observed at the above temperatures, respectively, in V(I) and V(III), a particularly marked anomaly in thermal expansion was observed at 261 K in a third V crystal, V(IIIA), whose hydrogen content was analyzed to be ~300 ppm by weight, significantly greater than that in V(I) and V(III). No other anomalies in the elastic constants between 4 and 300 K or in the thermal expansion between 4 and 370 K were observed.

A simple model based on the precipitation of interstitial hydrogen impurities in V, and capable of explaining the elastic-constant and thermal-expansion anomalies, may be constructed as follows. If $N(T)$ is the limit of solubility of H in V, and n_0 is the amount of H present in the crystal, then for $N(T)>n_0$ all of the hydrogen is in solution, while for $N(T)<n_0$ the fraction $n(T)=n_0-N(T)$ precipitates into an ordered hydride phase and forms "clusters" of V-H. From Westlake's work[2,3] we know that for V-H alloys $\ln N(T)=A-B/T$ where $A=5.828$, $B=1467$ K, T is in K, and $N(T)$ is in at.%. We define a transition temperature T_C, at which precipitation of hydrogen impurities starts, by $N(T_C)=n_0$. The behavior of

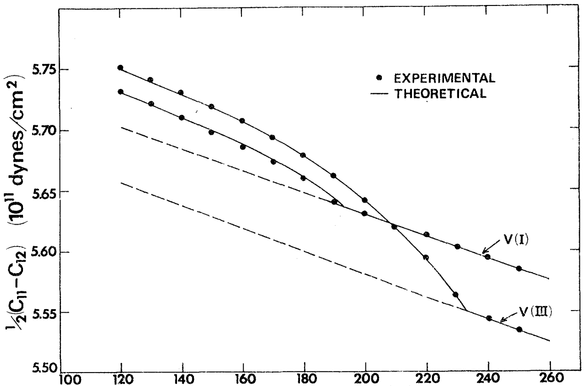

FIG. 1. Elastic constant $C' \equiv \frac{1}{2}(C_{11}-C_{12})$ as a function of temperature. 10-MHz shear waves, polarized along the $[1\bar{1}0]$ crystal axis, were propagated along the [110] axis. The theoretical curve was matched at 180 K for V(III); the curve for V(I) was obtained by use of Eq. (3).

$n(T)$ is then given by

$$n(T)=n_0\left[1-\exp\left\{-B\left(\frac{1}{T}-\frac{1}{T_C}\right)\right\}\right]$$
$$\equiv n_0G(T,T_C),\quad T<T_C,$$
$$n(T)=0,\quad T\geq T_C. \qquad (1)$$

If one expands the crystal free energy $F(T)=F_0(T)+F_1(T)n(T)$, in terms of $n(T)$, where F_0 is the crystal energy with no hydride precipitate and F_1 the bulk free energy of the hydride phase, one obtains for the elastic constants, to first order in $n(T)$,

$$C_{ij}(T)=\frac{\partial^2F(T)}{\partial e_i\partial e_j}=C_{ij}{}^0(T)+\gamma_{ij}n_0G(T,T_C), \qquad (2)$$

where the e_i are the strains and $C_{ij}{}^0(T)$ is the elastic constant under conditions of no V-H precipitation and is linear in T in this temperature range. γ_{ij} is a property of bulk V-H and should be the same for all V crystals. Thus if one evaluates $(\gamma_{ij}n_0)_1$ for crystal 1 with transition temperature T_{C1}, then $(\gamma_{ij}n_0)_2$ for any other crystal with transition temperature T_{C2} is given by

$$(\gamma_{ij}n_0)_2=(\gamma_{ij}n_0)_1\exp\left\{-B\left(\frac{1}{T_{C2}}-\frac{1}{T_{C1}}\right)\right\}. \qquad (3)$$

The application of this model to the elastic constant C' in V(I) and V(III) is shown in Fig. 1. The close agreement serves to identify hydrogen as the impurity responsible for the observed anomalies. The difference in $C_0'(\mathrm{I})$ and $C_0'(\mathrm{III})$ may be attributed to the larger impurity concentration (other than hydrogen) in V(I).[4] The theory presented here makes no assumption about $C_0'(T)$ other than its linearity. The theoretical curve for V(I) has no free parameters to match experiment. This is a strong indication of the validity of the present theory. The relatively crude matching of theory to experiment used here could tolerate an error in B/T_C of 10% and still produce a reasonable fit. This error could be reduced by using a better technique for determining γ_{ij} and T_C. Since it is known that other species of gaseous interstitials must be present in V in concentrations greater than 1000 ppm by weight to produce any precipitation phenomena,[5] the 10% possible error does not affect the identification of hydrogen as the culprit.

The lattice parameter of the V-H precipitate is larger than that of the host V lattice.[6] Applying the impurity precipitation model described above, one obtains an expression for the crystal volume, to first order in $n(T)$:

$$V(T)=V_0(T)+\beta n(T), \qquad (4)$$

where V_0 is the crystal volume with no precipitate present and β is in units of volume. Using the expressions for $n(T)$ given in Eq. (1), Eq. (4) is found to give an excellent fit to the experimental thermal expansion curve in the V single crystals.

The simple impurity-precipitation theory described above is deficient in explaining the experimentally observed effects in at least two respects. The theory predicts that T_C is unique for each crystal and that the slope of $C_{ij}(T)$ at T_C is discontinuous. It is found experimentally, however, that it is possible to "supercool" the V-H "solution" by rapid cooling through the transition and thereby to shift the transition temperature by as much as 10 K. Under conditions of rapid cooling, also, it is found that the transition, normally continuous, sharpens appreciably and tends to become discontinuous. The continuity of slope can be attributed to fluctuations in the local density of hydrogen interstitials at temperatures slightly above T_C. There will always be a certain fraction of the interstitials in the unstable and less probable "excited state" which, for $T>T_C$, is the precipitate state. If the crystal is cooled rapidly through T_C, the rate of nucleation of V-H precipitate may be too slow to keep the crystal in thermodynamic equilibrium and "supercooling" results.

The linewidth of the NAR $\Delta m=\pm2$ transition in Ta from 50 to 300 K is shown in Fig. 2. The existence of two NAR lines, one narrow and one

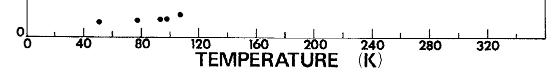

FIG. 2. Linewidth of the $\Delta m=\pm2$ transition in Ta No. 2 as a function of temperature. 10.848-MHz compressional waves (at $T=77$ K), propagated along [110] axis. Magnetic field $H_0=10.532$ kOe oriented parallel to [110] axis.

broad, at low temperatures is attributed by us to the coexistence of regions of pure Ta and of tantalum-impurity atom precipitates. Although ordering effects of interstitial atoms in tantalum-interstitial atom alloys previously have been observed,[7-9] in the present case the concentrations of interstitial atoms were significantly lower (estimated to be: N, <40; O, <100; H, ≤20; C, <40, in ppm).

The large, sharp maxima seen at 142, 185, 205, and 230 K in Fig. 2 may be qualitatively understood as due to ordering transitions of several impurity species. The differing lattice parameters of Ta and of Ta–interstitial-atom precipitate produce large strains at the boundaries of precipitate "clusters." Near a transition temperature clusters are rapidly fluctuating in size, and large numbers of Ta nuclei "see" the cluster boundaries. It is known that the linewidth of the NAR line in Ta is markedly dependent on strains present in the lattice.[10,11] This strain sensitivity of the linewidth, combined with the density fluctuations near a transition temperature, produces a maximum in the NAR linewidth.

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PHOTOLUMINESCENCE OF METALS

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Radiative recombination in gold, copper, and gold-copper alloys has been observed arising from transitions between electrons in conduction-band states below the Fermi level and holes in the *d* bands generated by optical excitation.

The first observation of optically excited radiative recombination of electrons and holes in metals is reported here. This emission involves states near the Fermi energy, in contrast to the soft-x-ray emission in which the excited holes are in the deep-lying bands. The noble metals gold and copper were studied as well as gold-copper alloys, but similar results should be observed in other metals.

The luminescence was excited both by an argon-ion laser which produced in excess of 2 W cw in either the 4880- or the 5145-Å line and by a high-pressure Hg arc lamp from which the 3000- to 4000-Å emission bands were used. Samples were in the form of ingots, single-crystal slices, or evaporated films. The spectra did not seem to be dependent on the type of sample used. Measurements were made at temperatures from 5 to 300°K. Standard Raman spectroscopy techniques were used to detect the emitted light and are described elsewhere.[1]

Figure 1 shows the luminescence spectra of gold at 300 and 10°K and copper at 300°K with the excitation source being the 4880-Å argon laser line. The emission spectra were totally unpolarized and did not vary with polarization of the incident laser beam which is consistent with luminescence from cubic cyrstals. The spectrum on the long-wavelength side is cut off by the strong absorption near the plasma edge while the short-wavelength side is limited by the energy available from the pumping source. The emission tail on the high-energy side of the laser occurs from thermal smearing of the electron and hole distributions and in the case of gold is seen to disappear at low temperature. In order to make