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**Abstract.** Sound velocity measurements carried out between 10 and 300 K in a $Pd_{85}Pt_{15}$ single crystal at 0 and 0.29 H contents for five different propagation modes, have shown that $C'$, $C_{44}$ and $C_T$ are strongly decreased by $H$ loading $(C_T = \frac{1}{3}(C_{11} - C_{12} + C_{44}))$. Smaller relative changes are observed for longitudinal modes. The bulk modulus as well as the anisotropy factor turn out to be increased by $H$ impurities. The Debye temperature at absolute zero is found to be $271 \pm 5$ K for $n = 0$ and $264 \pm 5$ K for $n = 0.29$.

## 1. Introduction

The elastic constant behaviour of 3d, 4d and 5d transition elements of the fifth (V, Nb, Ta) and tenth (Pd, Pt) columns has attracted much attention in the last few years, mainly because of an anomalous temperature dependence, which is particularly evident in the trigonal shear constant $C_{44}$ (Rayne 1960, Ashkenazi et al 1978, Nygren and Leisure 1988). Such an anomalous behaviour manifests itself in an upward concavity $C_{ij}(T)$ curves, which for $C_{44}$ of Pd is also associated with a pronounced minimum occurring below room temperature (Rayne 1960). This anomalous temperature dependence of $C_{ij}$ is generally believed (Peter et al 1977) to be related to some common features of the electron band structure of V, Nb, Ta, Pd and Pt. These consist in the existence of a narrow peak in the density of states of the d-band, with the Fermi level situated just above the top of the density of states peak, and in the fact that the Fermi surfaces contain closed and open sheets.

Following the line of some previous investigations in Nb (Mazzolai and Birnbaum 1985) and Pd/Ag alloys (Mazzolai et al 1983), the main aim of this work is that of examining the nature of the changes of the elastic constants induced by H. This is an extension of a previous anelastic investigation carried out in policrystalline material, to study hydrogen mobility and hydrogen ordering processes (Mazzolai et al 1987).

## 2. Experimental

A $Pd_{85}Pt_{15}$ single crystal supplied by Metals Research has been oriented and spark-erosion cut to have two pairs of parallel faces coinciding with (110) and (111) crystal planes. The specimen faces were parallel within $10^{-5}$ rad. After polishing the specimen was annealed at 600 °C for three hours at a pressure of $7 \times 10^{-6}$ torr. An H content $n$

$(n = \text{H}/(\text{Pd} + \text{Pt}))$ equal to 0.29 atomic was introduced electrolitically. Overall H losses, which were gravimetrically monitored between subsequent measurement runs, were found to be lower than 0.003 at.%.

The density was measured by the hydrostatic balance method and was found to be 13.64 g/cm$^3$ in the annealed state and 12.94 g/cm$^3$ after hydrogen loading. The echo-overlap method (Papadakis 1964) was used to obtain the ultrasonic velocity, and consequently the elastic constants. Five different modes were used, whose appropriate relationships between the ultrasonic velocity, $u$, and the three elementary elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ are the following:

$$\rho u_{[110]}^2 = \tfrac{1}{2}(C_{11} + C_{12} + 2C_{44}) = C_{\text{L}}$$
$$\rho u_{[111]}^2 = \tfrac{1}{3}(C_{11} + 2C_{12} + 4C_{44}) = C^* \tag{1}$$

$$\rho u_{[110]}^{2[1\bar{1}0]} = \tfrac{1}{2}(C_{11} - C_{12}) = C'$$
$$\rho u_{[110]}^{2[001]} = C_{44} \tag{2}$$
$$\rho u_{[111]}^2 = \tfrac{1}{3}(C_{11} - C_{12} + C_{44}) = C_{\text{T}}$$

In the above relations the lower and the upper indices indicate the propagation and the polarisation directions, respectively. For the last mode the polarisation direction was an arbitrary one in the (111) plane. Either the nonaq. stopcock grease or honey served as satisfactory bonds of the quartz transducer down to liquid helium temperatures. An Au + 0.07 at.% Fe and cromel thermocouple was used to monitor the temperature. The data have been corrected for thermal expansion by taking for the temperature coefficient $\alpha$ the values of pure Pd (Abbenseth and Wipf 1980).

## 3. Results

Figure 1 shows the experimental values $(C_{ij}^{\text{R}})$ of the elastic constants of the Pd$_{85}$Pt$_{15}$ crystal as measured on cooling both before and after hydrogenation. In the H-free state of the material the elastic constant $C_{44}$ shows a slight upward concavity, which is reminiscent of the well known more evident minimum observed in pure Pd (Rayne 1960). All the other investigated elastic constants show a normal temperature behaviour, with a negative curvature towards the temperature axis.

It is noted that hydrogenation to an H level of 0.29 induces a large decrease in all the measured elastic constants over almost the entire temperature range. Any anomalous behaviour of the temperature dependence of $C_{44}$ is eliminated by H-charging. The temperature dependence of $C_{ij}$ appears to be enhanced by H. This is partly due to the presence of a relaxation process which gives rise to an attenuation maximum at about 225 K (for $f = 10$ MHz) and which affects the elastic constants above about 150 K. The relaxation contribution to the elastic constant decrease has been calculated by using an approximate procedure suggested by Bordoni and Maschio (1982). A detailed discussion of the relaxation features will be presented elsewhere. In figure 1 the unrelaxed values $C_{ij}^{\text{U}}$ of the elastic constants obtained after subtraction of the relaxation contribution are also plotted.

Measurements have also been made on heating, the results are substantially the same as those on cooling. This suggests that no $\alpha \Leftrightarrow \beta$ phase transition takes place during the

**Table 1.** Estimated values of $C_{11}$, $C_{12}$, $B$ and of the anisotropy ratio $A$ ($A = C'/C_{44}$) in units of Pa, for $n = 0$.

| $T$ (K) | $C_{11}$ | $C_{12}$ | $B$ | $A$ |
|---|---|---|---|---|
| 20.0 | 2.561 | 1.843 | 2.083 | 0.4033 |
| 30.0 | 2.561 | 1.840 | 2.081 | 0.4030 |
| 40.0 | 2.560 | 1.841 | 2.081 | 0.4029 |
| 50.0 | 2.560 | 1.841 | 2.081 | 0.4029 |
| 60.0 | 2.559 | 1.842 | 2.081 | 0.4023 |
| 70.0 | 2.557 | 1.841 | 2.080 | 0.4022 |
| 80.0 | 2.555 | 1.840 | 2.078 | 0.4012 |
| 90.0 | 2.551 | 1.838 | 2.076 | 0.4001 |
| 100.0 | 2.548 | 1.835 | 2.073 | 0.3985 |
| 110.0 | 2.543 | 1.833 | 2.070 | 0.3972 |
| 120.0 | 2.539 | 1.833 | 2.068 | 0.3965 |
| 130.0 | 2.538 | 1.833 | 2.068 | 0.3961 |
| 140.0 | 2.535 | 1.832 | 2.066 | 0.3953 |
| 150.0 | 2.531 | 1.830 | 2.064 | 0.3938 |
| 160.0 | 2.526 | 1.827 | 2.060 | 0.3923 |
| 170.0 | 2.522 | 1.825 | 2.057 | 0.3911 |
| 180.0 | 2.519 | 1.824 | 2.056 | 0.3903 |
| 190.0 | 2.516 | 1.823 | 2.054 | 0.3895 |
| 200.0 | 2.512 | 1.822 | 2.052 | 0.3884 |
| 210.0 | 2.507 | 1.819 | 2.049 | 0.3871 |
| 220.0 | 2.503 | 1.817 | 2.046 | 0.3857 |
| 230.0 | 2.499 | 1.814 | 2.043 | 0.3845 |
| 240.0 | 2.496 | 1.813 | 2.041 | 0.3836 |
| 250.0 | 2.493 | 1.812 | 2.039 | 0.3829 |
| 260.0 | 2.490 | 1.809 | 2.037 | 0.3820 |
| 270.0 | 2.486 | 1.807 | 2.034 | 0.3807 |
| 280.0 | 2.482 | 1.803 | 2.030 | 0.3794 |
| 290.0 | 2.479 | 1.801 | 2.027 | |

measurement cycle, probably because below the temperatures of the $\alpha \Leftrightarrow \beta$ solvus the H mobility is too low for the ordering process to occur.

The observations described here are somewhat different from those reported for the $\alpha'$ Pd hydride phase at the hydrogen levels 0.66 and 0.70 (Nygren and Leisure 1988). In this last case it has been found that the elastic constant $C'$ is increased while the temperature dependence of $C'$, $C_{44}$ and $C_{11}$ is decreased by H loading.

From the experimental data of $C'$, $C_{44}$, $C_L$, $C^*$ and $C_T$, the values of $C_{11}$, $C_{12}$, $B$ and the anisotropy ratio $A(A = C'/C_{44})$ have been calculated, by using four different combinations of the measured quantities. The results are consistent with one another and their mean values are listed in tables 1 and 2. Differently from all the other elastic constants, $C_{12}$ and $B$ are found to be higher in H-loaded than in H-free material.

## 4. Discussion

One of the most interesting observations made in figure 1 is that before hydrogenation the temperature dependence of $C_{ij}$ is normal perhaps with the exception of $C_{44}$ which, however, only shows a hardly noticeable upward concavity. This indicates that Pt,
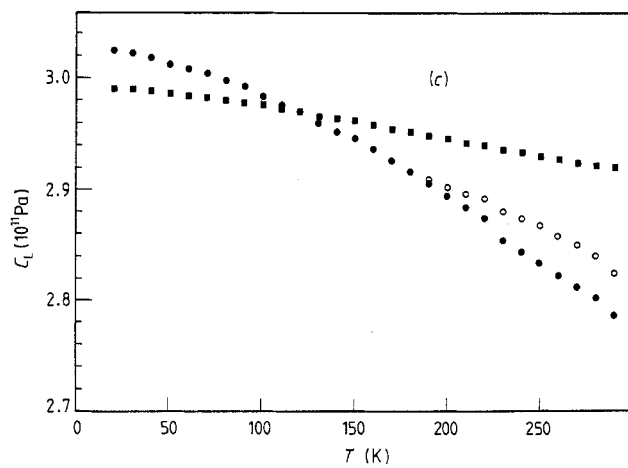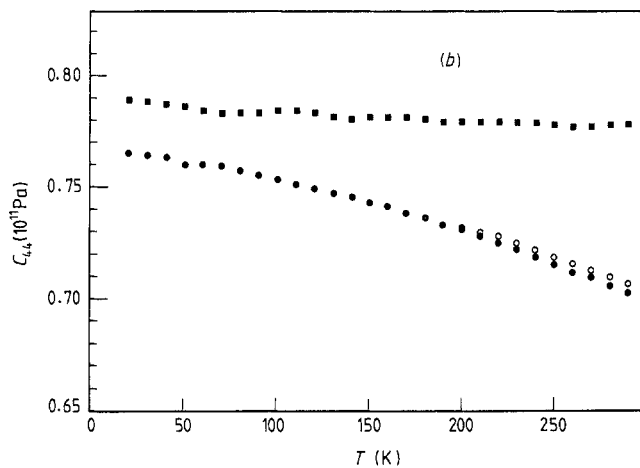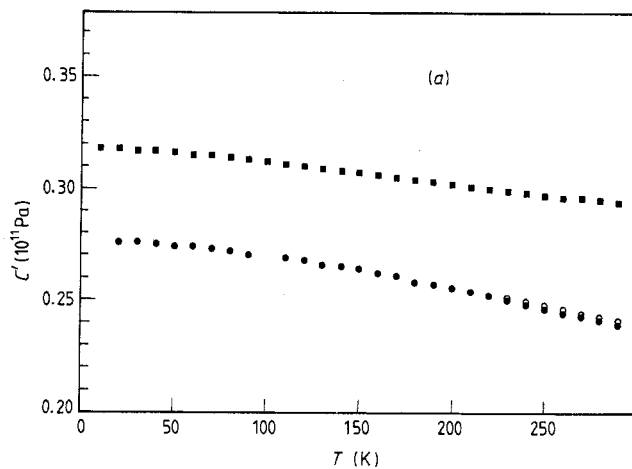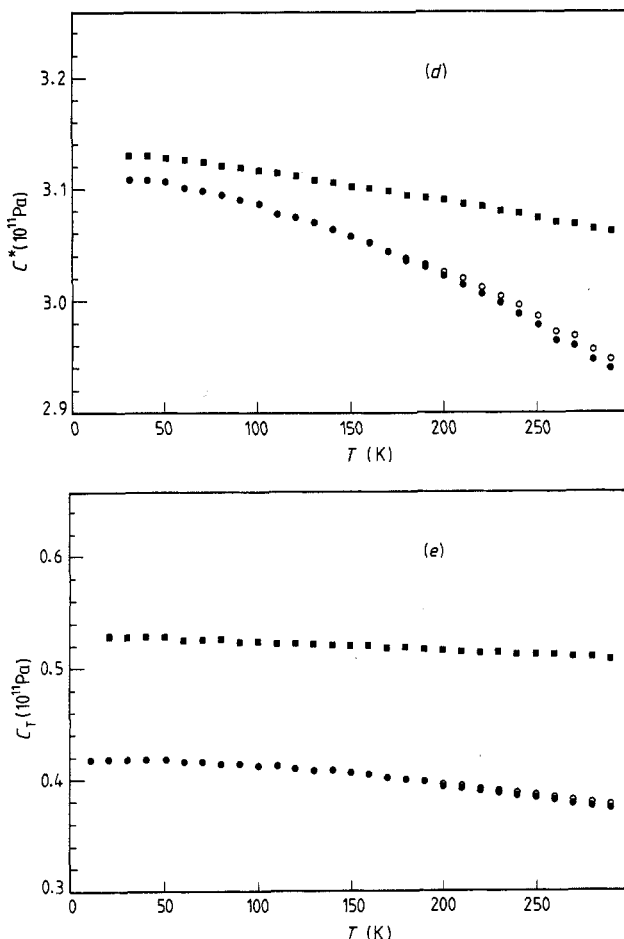
**Figure 1.** Temperature dependence of the relaxed ($C^R$; ●) and unrelaxed ($C^U$; ○) elastic constants: (a) $C'$; (b) $C_{44}$; (c) $C_L$; (d) $C^*$; (e) $C_T$. ○, ●, $n = 0.29$; ■, $n = 0$.

contrary to what might have been expected, is quite effective in modifying the band structure and/or the density of states at the Fermi level of Pd.

In view of the basically normal behaviour of the elastic constants of Pd/Pt/H alloys, theories less elaborated than that of Peter *et al* 1977, such as those of Fuchs and Wills 1935 and de Launay 1956, are probably adequate to account for some of the main features of the present results.

The values of the anisotropy factor $A$ are found to be far from unity, as it happens for most of the fcc metals and alloys. Surprisingly, however, the anisotropy is higher in the H loaded than in the H free state of the material. An opposite behaviour is shown by the $\alpha'$ solid solution phase of Nb, which even becomes perfectly isotropic ($A = 1$) for an H content $n = 0.50$ (Mazzolai and Birnbaum 1985a). This suggests that the $\alpha'$ hydride of Pd/Pt alloys is not an ideal solid solution but it is rather associated with a certain degree of directional short-range order. $C_{12}$ and $C_{44}$ do not obey the Cauchy relation ($C_{12} = C_{44}$), thus showing that the central force model does not apply. According to Fuchs and de Launay the failure of the Cauchy relation is to be attributed to the

**Table 2.** Estimated values of $C_{11}$, $C_{12}$, $B$ and of the anisotropy ratio $A$ ($A = C'/C_{44}$) in units of Pa, for $n = 0.29$.

| $T$ (K) | $C_{11}$ | $C_{12}$ | $B$ | $A$ |
|---|---|---|---|---|
| 20.0 | 2.539 | 1.929 | 2.132 | 0.3611 |
| 30.0 | 2.536 | 1.925 | 2.129 | 0.3612 |
| 40.0 | 2.531 | 1.922 | 2.126 | — |
| 50.0 | 2.529 | 1.919 | 2.122 | 0.3610 |
| 60.0 | 2.524 | 1.915 | 2.118 | 0.3605 |
| 70.0 | 2.518 | 1.913 | 2.115 | 0.3594 |
| 80.0 | 2.514 | 1.913 | 2.113 | 0.3594 |
| 90.0 | 2.510 | 1.911 | 2.112 | 0.3586 |
| 100.0 | 2.506 | 1.908 | 2.107 | — |
| 110.0 | 2.495 | 1.907 | 2.103 | 0.3581 |
| 120.0 | 2.488 | 1.906 | 2.100 | 0.3575 |
| 120.0 | 2.478 | 1.904 | 2.096 | 0.3569 |
| 140.0 | 2.472 | 1.902 | 2.092 | 0.3563 |
| 150.0 | 2.463 | 1.900 | 2.088 | 0.3552 |
| 160.0 | 2.454 | 1.898 | 2.083 | 0.3539 |
| 170.0 | 2.445 | 1.895 | 2.079 | 0.3533 |
| 180.0 | 2.434 | 1.892 | 2.073 | 0.3515 |
| 190.0 | 2.426 | 1.889 | 2.068 | 0.3507 |
| 200.0 | 2.413 | 1.887 | 2.062 | 0.3493 |
| 210.0 | 2.403 | 1.884 | 2.057 | 0.3488 |
| 220.0 | 2.393 | 1.881 | 2.052 | 0.3476 |
| 230.0 | 2.374 | 1.879 | 2.044 | 0.3465 |
| 240.0 | 2.363 | 1.874 | 2.037 | 0.3455 |
| 250.0 | 2.351 | 1.869 | 2.030 | 0.3442 |
| 260.0 | 2.343 | 1.861 | 2.022 | 0.3432 |
| 270.0 | 2.332 | 1.861 | 2.018 | 0.3420 |
| 280.0 | 2.325 | 1.856 | 2.012 | 0.3417 |
| 290.0 | 2.308 | 1.852 | 2.004 | 0.3409 |

conduction electrons, which contribute to the bulk modulus and to the not pure shear elastic constants a big positive term, $B_e$, given by:

$$B_e = C_{12} - C_{44} \qquad (3)$$

In the case of the H loaded material, $B_e$ will include the contribution of H interstitials. In figure 2 the relative changes $\Delta C_{ij}/C_{ij}$ induced by H are plotted as a function of temperature. It is worth noting that, while the pure shear elastic constants $C_{44}$, $C'$ and $C_T$ show a marked negative change, only minor variations and in most of the cases of positive sign, occur in the other elastic constants. This is clearly due to the positive contribution $B_e$ of the electron gas and of $H$ interstitials to the not pure shear elastic constants.

In the Born–Von Karman model the elastic force constants $\alpha_1$ and $\alpha_2$ between first and second nearest-neighbours are given by (de Launay 1956):

$$\alpha_1 = aC_{44}$$
$$\alpha_2 = a/4(C_{11} - C_{12} - C_{44}) \qquad (4)$$
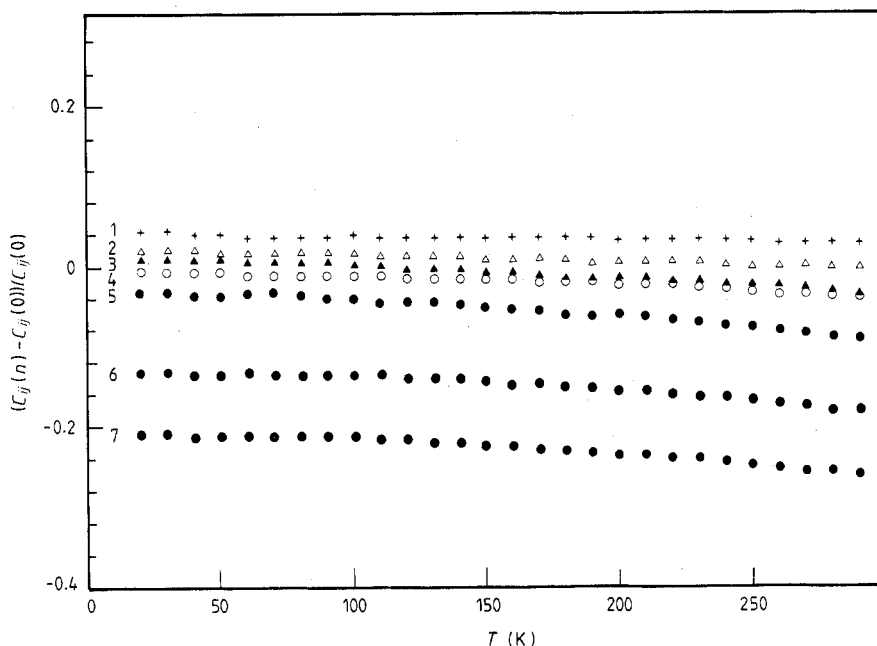
where $a$ is the lattice parameter.

**Figure 2.** Relative changes $\Delta C_{ij}/C_{ij}$: 1, $C_{12}$; 2, $B$; 3, $C_L$; 4, $C^*$; 5, $C_{44}$; 6, $C'$; 7, $C_T$.

**Table 3.** Force constants and relative changes of $Pd/Pt/H_n$ alloys at 20 K.

| $n$ | $\alpha_1$ $(N/m)$ | $\alpha_2$ $(N/m)$ | $\|\Delta\alpha_1/\alpha_1\|$ | $\|\Delta\alpha_2/\alpha_2\|$ |
|---|---|---|---|---|
| 0.00 | 30.56 | −0.069 | | |
| 0.29 | 30.17 | −0.092 | 0.013 | 0.33 |

The values of $\alpha_1$ and $\alpha_2$ as deduced at 20 K from the present measurements are listed in table 3, together with the relative changes. As it is seen the interaction between second nearest-neighbours is relatively small and slightly repulsive. H impurities decrease the attractive force between first nearest neighbours and increase the repulsive forces between second nearest-neighbours, thus giving rise to a generalised softening effect.

As it is known the Debye temperature $\theta$ can be deduced at low temperatures ($T \leqslant \theta/12$) from the elastic data. The average values of $\theta$ extrapolated towards the absolute zero, as obtained by applying Marcus method (Alers 1965) and by using four different combinations of the measured $C_{ij}$, are $271 \pm 5$ K ($n = 0$) and $264 \pm 5$ K ($n = 0.29$).

## 5. Conclusions

As discussed in the previous section, alloying of Pd with Pt gives rise to unexpected substantial changes in the temperature dependence of $C_{ij}$. The conclusion can be drawn that the increased anisotropy of the H loaded material, as well as the marked difference observed in the relative changes between the pure and not pure shear elastic constants, is basically due to the contribution of electrons and H interstitial compressibilities. The

major effect of H on the ion lattice is to substantially increase the repulsive forces between second nearest-neighbours.

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