Dechanneling of α particles by hydrogen atoms in palladium

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Dechanneling of α particles by hydrogen atoms dissolved in palladium has been studied by the method of channelography. The exponential law for the variation of the dechanneling yield versus concentration of defects has been verified for the first time in a metal. A dechanneling cross section for hydrogen atoms in palladium has been deduced from the measurement and found equal to $(5.7 \pm 2.6) \times 10^{-3}$ Å^2. The effect is primarily attributed to the obstruction of the channels by the protons.

I. INTRODUCTION

For the first time, the exponential law for the attenuation of channeled particles has been verified for a point defect in a metal. Specifically, the relation (Ref. 1)

$$\chi = 1 - e^{-\bar{\sigma} C t} \tag{1}$$

has been found valid for the dechanneling of α particles by hydrogen atoms dissolved in palladium. In this expression, χ is the yield of the dechanneling of particles by the defects, $\bar{\sigma}$ is the dechanneling cross section of the defects, C is their volumetric concentration, and t is the thickness of the sample. Concurrently, we measure $\bar{\sigma} = (5.7 \pm 2.6) \times 10^{-3}$ Å^2 which is in good order-of-magnitude agreement with the theoretical value of 1.1×10^{-2} Å^2 found by Matsunami and Itoh[2] for 1.5-MeV protons dechanneled by displaced atoms in ⟨100⟩ rows of KCl.

The dechanneling effect is generally interpreted in terms of scattering either by a channel *obstruction* (typical example: stacking fault[3]), or by a *strain field* surrounding the defect (typical example: dislocations[4]), or simultaneously by obstruction *and* deformation (typical example: Guinier-Preston zones[5]). The experimental value we have found for $\bar{\sigma}$ is very small compared to the dechanneling cross section of dislocations.[6] This is an indication that dechanneling by hydrogen atoms in palladium is merely due to the obstruction of the channel rather than to a possible deformation of the channel in the vicinity of the defect. This idea is also consistent with the extremely small formation volume of hydrogen in palladium, which one of us[7] has measured and found equal to $(0.08 \pm 0.02)\ \Omega$, Ω being the atomic volume of palladium.

II. EXPERIMENTAL METHOD

A. Samples

The samples were made of polycrystalline strips 12 μm thick, 60 mm long, and 10 mm wide. The purity was 99.95%. The mean grain diameter of the samples was an order of magnitude larger than the thickness.

Hydrogen was introduced in palladium by heating the sample to about 700 °C in a brass chamber containing an atmosphere of helium-hydrogen gas having a total pressure of a few bars. The partial pressure of hydrogen could be varied from 0 to a few Torrs. The helium-hydrogen quenching mixture was kept cold by immersion of the brass chamber in liquid nitrogen. By switching off the heating current in the sample, the equilibrium concentration of hydrogen in palladium was quenched in. Depending on the partial pressure of hydrogen in the chamber and the quench rate, a certain concentration of hydrogen atoms was maintained in solution. This concentration was measured at 77 K by means of the change of electrical resistivity of the specimen after the quench. The dependence of electrical resistivity to hydrogen concentration had been previously established at room temperature under equilibrium conditions.[8] The deviation from Matthiessen's rule was determined and taken into account in the present measure.

Great care was taken to avoid the nucleation of the β phase of the palladium-hydrogen system.[9] This phase, which has the same fcc structure as palladium, has a lattice parameter much larger than that of the α phase. Any presence of β-phase nuclei would thus induce some stress and probably some deformation due to the local cold work. This generation of dislocations would obviously make more difficult to observe, or would even conceal the dechanneling effect of hydrogen.

The concentrations obtained with this technique were typically on the order of a few percent. The hydrogen atoms dissolved in palladium anneal out at room temperature when the sample is kept in air for a period of a few hours.

B. Channelography

Measurements of dechanneling yield were made by the method of *channelography*. This technique has been described elsewhere.[1,10] Briefly, a

polycrystalline sample is placed in contact with ^{241}Am deposited on the surface of a ribbon. The sample thickness permits only channeled particles to emerge from the sample. Each grain presents to the isotropic flux of α particles its own set of close-packed planes. Only those planes making a small angle with the normal to the sample surface can act as channeling planes. Consequently, the rate of channeled particles varies from one grain to another, since the "effective" thickness of each grain depends on its orientation. The channeled particles are recorded on a collector made of a nitrate cellulose foil. Each particle impact is made visible by the preferential chemical attack of NaOH in these damaged regions. Each channeled particle track so revealed is, in general, seen as a domain a few microns in extent, and can thus be observed with an ordinary microscope.

All channelographs were made at 77 K. Immediately after the quench, the sample chamber was opened while in contact with a liquid-nitrogen bath and the sample placed between the americium source and the collector. These operations were performed in the nitrogen dry atmosphere just above the liquid-nitrogen bath. This procedure limited the sample temperature to no more than about 80 K well below the "anneal out" temperature of the hydrogen atoms. In addition, the dry-nitrogen atmosphere completely inhibited the formation of ice at the interfaces in the source-specimen-collector "sandwich." Obviously, the presence of ice at these locations would perturb considerably the transmission of α particles. This sandwich was then placed in the specimen chamber which was subsequently evacuated and maintained at 77 K during the time of exposure—typically 15 h. After obtaining the channelograph for the palladium-hydrogen system in this fashion, the specimen was then annealed to obtain the hydrogen-free state—later verified by an electrical resistivity measurement. The "hydrogen-free" channelograph was then made under exactly the same conditions as for the "palladium-hydrogen" channelograph; i.e. the temperature, vacuum, and exposure times were identical in the two cases.

C. Dechanneling yield

The measure of the dechanneling yield was made by counting the density n of tracks on the channelographs. The dechanneling yield χ is defined as

$$\chi = (n_0 - n_H)/n_0 \qquad (2)$$

where the subscripts 0 and H indicate respectively the density of tracks on the "hydrogen-free" and the "palladium-hydrogen" channelographs. It must be emphasized that χ measures only the dechanneling by hydrogen atoms. It does not include other effects such as thermal dechanneling or electronic multiple scattering[11] since the two channelographs 0 and H are made under exactly the same conditions (see Sec. IV).

The counting was performed by means of an optical microdensitometer. This apparatus measures the optical density d of transparent materials, d being the decimal logarithm of the opacity of the material. As mentioned earlier, since the rate of channeled particles varies from one grain to another, each grain appears as a region of certain contrast on the channelograph. d is measured on a total surface of 150 mm^2 on the channelograph and takes into account all the variation of contrast between the "images" of about 15 000 grains. Great care is taken to measure the densities d_0 and d_H at the same positions on the two channelographs so that the same grains are counted in the two cases. One determines $\chi' = (d_0 - d_H)/d_0$ which is due solely to the presence of the hydrogen atoms in palladium. It can be shown[7] that this χ' is the same as the χ defined by Eq. (2).

III. RESULTS

By adjusting the partial pressure of hydrogen gas, C was varied from 0 to 0.025 in atomic concentration. In this concentration range the resulting dechanneling yield χ was found to increase from 0 to 0.70.

Let us again consider Eq. (1)

$$\chi = 1 - e^{-\bar{\sigma} C t}\,, \qquad (1)$$

where (i) C is assumed to be uniform throughout the thickness (it is highly probable that the distribution of hydrogen atoms is uniform throughout the sample); (ii) $\bar{\sigma}$ is the dechanneling cross section averaged over all the channeling conditions of the particles (see Sec. IV); (iii) t is actually the "effective" thickness corresponding to every set of channeling planes for each grain. It has been shown for conditions quite similar to ours[6] that t "effective" is about 1.07 times the sample thickness. When using this correction one can be sure that the error on t is certainly inferior to 10%.

As a consequence of Eq. (1), a plot of $\ln(1-\chi)$ versus concentration C ought to be linear with the slope of the straight line equal to $\bar{\sigma} t$.

Figure 1 shows that, to a good approximation, the variation of $\ln(1-\chi)$ is, indeed, linear in the range of the experiment. From a linear fit to the data, one obtains

$$\bar{\sigma} = (5.7 \pm 2.6) \times 10^{-3}\ \text{Å}^2.$$

The fit to the data is made by means of a least-squares-type method. In the case of this experiment, the relative error in both $\ln(1-\chi)$ and C are estimated to be of the same order and equal to about 10%. Consequently, the usual least-squares fit cannot be used since it supposes that one of the

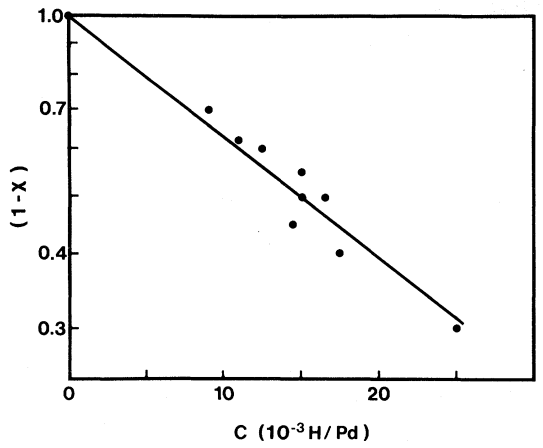

FIG. 1. Variation of $(1-\chi)$ (χ being the experimentally measured dechanneling yield) vs the atomic concentration C of hydrogen atoms dissolved in palladium.

variables is well known with respect to the other.

An analysis[12] similar to the least-squares method, but taking into account that in the linear relation $y=bx$ there is an error in both y and x, gives

$$b=\sum X_i y_i \Big/ \sum X_i^2 ,$$

with

$$X_i=(x_i/\sigma_x^2+y_i/\sigma_y^2)/(1/\sigma_x^2+b^2/\sigma_y^2),$$

where σ_x and σ_y are the standard deviations of x and y, respectively. We used an iterative method in which one starts by assigning an initial value to b. This value is used to calculate σ_x and σ_y, hence X_i. As can be seen above, X_i and y_i serve to determine a value for b. This determination of b is compared to the "starting" value of b assumed at the outset. When the two values of b are equal to within 1%, the calculation is assumed to be complete. The uncertainty in b was then evaluated by differentiation of the above relation with respect to x_i and y_i.

The uncertainty of $\pm 2.6\times 10^{-3}$ Å^2 in the measure of $\bar{\sigma}$ consists of the uncertainty in the slope $\bar{\sigma}t$ (± 2.0) and the uncertainty in t (± 0.6).

IV. DISCUSSION

A. Method

As expressed in Sec. II, our method is assumed to be purely differential and, consequently, gives a measure of the dechanneling effect of hydrogen impurities. This point can be made more precise with the following considerations. On the channelograph 0 ("hydrogen-free") we record the n_0 particles channeled through the sample in which two types of dechanneling occur: (i) by the "permanent defects" (dislocations, grain boundaries, etc...); (ii) by a multiple-scattering effect.

On the channelograph H (with hydrogen), the presence in the palladium crystal of hydrogen impurities leads to a decrease from n_0 to n_H in the number of channeled particles. When we assume that the dechanneling yield of hydrogen atoms is $(n_0-n_H)/n_0$, we suppose that the presence of hydrogen impurities does not modify the effects (i) and (ii) for the following reasons.

(a) The concentration of "permanent defects" could be modified by the treatment at 700 °C during which hydrogen atoms are introduced in the sample. This is not the case, as it has been verified by tests where hydrogen was replaced for the thermal treatment by helium gas. In such a test, within the experimental uncertainty, $n_0=n_{\mathrm{He}}$.

(b) The presence of hydrogen impurities certainly varies the dechanneling effect of multiple scattering as taken into account in channelograph 0. This variation Δ_{MS} comes from modifications in the thermal vibrations of palladium nuclei and of the electronic density of the crystal. We thus have to compare the order of magnitude of Δ_{MS} to the order of magnitude of the dechanneling effect of hydrogen itself.

We have compared firstly the orders of magnitude of this dechanneling effect of hydrogen and of the dechanneling yield by multiple-scattering events. We have evaluated $x_{1/2}$, the characteristic crystal thickness at which one-half of the initially channeled particles have been dechanneled by hydrogen impurities. We find $x_{1/2}=7\mu$m, which is of the same order of magnitude as the value of the same parameter measured for multiple scattering by Feldman and Appleton[11] in the case of MeV protons channeled in silicon and germanium, and even larger than the value of 1 μm found by Mory[13] for 1-MeV α particles in gold.

We assume that Δ_{MS} is proportional to the concentration of hydrogen impurities in palladium. The largest concentration in the present experiment is 2.5×10^{-2} H/Pd. As a consequence, Δ_{MS} is about 2.5×10^2 times smaller than the measured dechanneling effect of hydrogen.

Consequently, it can be concluded that our method is really differential.

B. Results

If all the conditions of channeling throughout the sample are considered, the dechanneling cross sections are essentially a function of the type $\{hkl\}$ of the channeling plane and of the energy E of the particle. That is,

$$\sigma=\sigma(\{hkl\}, E).$$

The *planes* involved in the present experiment are the close-packed $\{111\}$ planes of fcc palladium.

We have direct evidence of this feature owing to the presence, on the channelographs, of geometrical patterns[14] due to the numerous local inhomogeneities of the americium source. These patterns give the individual orientation of the grains as well as the family of channeling planes. In our case, the orientations are mostly ⟨111⟩ perpendicular to the surface of the samples, and the channeling planes are in an overwhelming proportion of the type {111}. As a consequence, the experimental value of $\bar{\sigma}$ essentially gives a measure of $\bar{\sigma}_{\{111\}}$.

As far as the *energy* is concerned, the measured value $\bar{\sigma}$ is an average over all the energies between the initial value (~4 MeV) and the final value (~0.7 MeV). It is interesting to compare our experimental averaging with the results of a calculation made in our laboratory.[15] This calculation is based upon the following considerations. It is known that hydrogen atoms are probably located at the octahedral sites of the palladium lattice, that is to say at equal distance from {111} planes. As $\bar{\sigma}$ is small (compared to the values found for dislocations, for instance Refs. 4 and 16), one can deduce that the dechanneling effect of hydrogen in palladium is probably of the obstruction type, and that the lattice is free of distortion. This obstruction has been described by a Rutherford-type interaction in which an α particle is scattered by a proton.

Results for the scattering cross section are in good agreement with the experimentally measured value of $\bar{\sigma} = 5.7 \times 10^{-3}$ Å^2. For the two extreme values of the energy the calculation yields

$\sigma(4\ \text{MeV}) = 2.5 \times 10^{-3}$ Å^2,

$\sigma(0.7\ \text{MeV}) = 6 \times 10^{-3}$ Å^2.

Such good agreement confirms our description of dechanneling in terms of obstruction.

V. CONCLUSION

The method of channelography has permitted the measurement of the dechanneling cross section of a hydrogen atom for α particles channeled between {111} planes of palladium. As the α-particle flux traverses the entire thickness of the crystal, the value of $\bar{\sigma}$ obtained is representative of hydrogen impurity dechanneling in the bulk of the sample. In addition, we emphasize that this differential technique eliminates systematic effects previously referred to.

It seems obvious that the dechanneling effect is an efficient tool for studying crystal defects, as other types of dechanneling experiments have already shown.[16,17]

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