DISLOCATION-HYDROGEN CORRELATION IN METALS*

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DISLOCATION-HYDROGEN CORRELATION IN METALS

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We present a method using SANS experiments to measure correlation between dislocations and absorbed hydrogen in metals. The technique involves sequential measurements first on a metal with dislocation networks, then two further measurements on the same sample infused with deuterium and normal hydrogen. SANS experiments on metals with dislocation networks have been performed a number of times and some results have appeared in the literature. We have computed estimates of the contribution of absorbed hydrogen and deuterium to SANS cross sections. The results show that we can expect to see the hydrogen contribution in the SANS cross section and see any possible correlations of the hydrogen positions and the dislocations.

Introduction

Our objective is to devise an experiment to measure the correlations between hydrogen and dislocations in a metal using small angle neutron scattering (SANS). Here we are going to show that the contributions of dissolved hydrogen appear to be large enough to measure with SANS. The forward scattering from a metal containing dislocations will be enhanced when hydrogen is added. If correlations between dislocations and hydrogen exist they will be seen in this additional scattering. SANS from dislocations has been measured (Epperson et al, 1976, Taglauer, 1968, and Christ, 1964). The range of Q values and dislocation densities in copper are shown in Table 1. All three experiments used copper samples deformed to high dislocation densities. In each, the forward scattering at low Q showed a $1/Q^3$ dependence, as expected from the theoretical work by Seeger and Kroner (Seeger and Kroner, 1959) and by Atkinson and Hirsch (Atkinson and Hirsch, 1958).

Measurements of the solubility of hydrogen in deformed palladium have been made (Flanagan et al, 1976, Flanagan and Kishimoto, 1983, and Kirchheim, 1981). These show that the hydrogen solubility increases when the metal lattice is deformed substantially. In Table 2 we present the solubility enhancement (defined as the hydrogen concentration in the deformed metal divided by the hydrogen concentration in the annealed metal) for palladium. This increased solubility of hydrogen in

palladium with large dislocation densities is thus far the strongest evidence we have that there exists a correlation between dissolved hydrogen and dislocations. This evidence says nothing about the possible spatial correlations between the hydrogen positions and the dislocations in palladium.

In the two tables discussed in this section, examples of dislocation forward scattering from copper and enhanced hydrogen solubility in deformed palladium are given. An enhancement in the dissolved hydrogen concentration will produce an enhanced SANS signal from the hydrogen. The SANS results of Epperson et al (Epperson et al, 1976), Taglauer (Taglauer, 1968), and Christ (Christ, 1964) are all for high dislocation densities ($\sim 10^{11} \text{cm}^{-2}$). Since a high dislocation density seems to be a prerequisite for measuring dislocation forward scattering, a high dislocation density would also seem to be necessary to measure the enhanced, dissolved hydrogen forward scattering. This point is illustrated later where hydrogen cross sections are estimated.

Scattering Theory

The total microscopic neutron scattering cross section per steradian from a deformed metal is given by;

$$S_{m+L}(Q) = \left| \sum_m^N a_m e^{iQ \cdot R_m} \right|^2 \quad (1)$$

where $Q = k - k'$, k and k' are the incident and scattered wave vectors, respectively, a_m and R_m are the m^{th} metal atom scattering length and position, respectively, N is the total number of metal atoms exposed to the neutron beam, and L denotes the presence of dislocations in the metal lattice.

Now consider a deformed metal sample with hydrogen loaded into the matrix. We assume that the dissolved hydrogen does not change the dislocation density or structure. If we also assume that deuterium dissolves into the metal exactly the same way that hydrogen does, we can write the SANS cross sections for deformed metal loaded with hydrogen ($S_{m+L+H}(Q)$) and that loaded with deuterium ($S_{m+L+D}(Q)$) as;

$$S_{m+L+H}(Q) = S_{m+L}(Q) + \frac{N' \sigma_{in}^H}{4\pi} + \frac{\sigma_{coh}^H}{4\pi} \left\langle \sum_{m,m'}^N e^{iQ \cdot (r_m - r_{m'})} \right\rangle + \left\langle 2 \sum_{m,m'}^N a_m b_{m'} \text{Re} [e^{iQ \cdot (r_m - R_m)}] \right\rangle \quad (2a)$$

$$S_{m+L+D}(Q) = S_{m+L}(Q) + \frac{N' \sigma_{in}^D}{4\pi} + \frac{\sigma_{coh}^D}{4\pi} \left\langle \sum_{m,m'}^N e^{iQ \cdot (r_m - r_{m'})} \right\rangle + \left\langle 2 \sum_{m,m'}^N a_m c_{m'} \text{Re} [e^{iQ \cdot (r_m - R_m)}] \right\rangle \quad (2b)$$

where $S_{m+L}(Q)$ represents the background scattering from the deformed metal sample and 'Re' refers to

the real part. The second term on the RHS of equations (2) is due to incoherent scattering from hydrogen (or deuterium), the third term results from hydrogen-hydrogen (or deuterium-deuterium) pair correlations, and the fourth term results from hydrogen-dislocation (or deuterium-dislocation) correlations. In the above equations r_m and $r_{m'}$ are the hydrogen or deuterium atomic positions, and N is the total number of hydrogen or deuterium atoms dissolved in the sample. Also b_m and c_m are the scattering lengths for the m^{th} hydrogen and deuterium atom, respectively. σ_{in} and σ_{coh} are the microscopic incoherent and coherent scattering cross sections, respectively, for hydrogen or deuterium as labeled, and $\langle \dots \rangle$ means the enclosed quantity is averaged over many dislocations.

If hydrogen and deuterium incoherent scattering can be neglected in the low Q range (this is justified in the next section) equations 2 are rewritten as;

$$S_{m+L+H}(Q) = S_{m+L}(Q) + \frac{\sigma_{\text{coh}}^H}{4\pi} \left\langle \sum_{m,m'}^{N'} e^{iQ \cdot (r_m - r_{m'})} \right\rangle + b \left\langle 2 \sum_{m,m'}^{NN'} a_m \text{Re}[e^{iQ \cdot (r_m - R_m)}] \right\rangle \quad (3a)$$

$$S_{m+L+H}(Q) = S_{m+L}(Q) + b^2 P(Q) + b I(Q) \quad (3b)$$

$$S_{m+L+D}(Q) = S_{m+L}(Q) + \frac{\sigma_{\text{coh}}^D}{4\pi} \left\langle \sum_{m,m'}^{N'} e^{iQ \cdot (r_m - r_{m'})} \right\rangle + c \left\langle 2 \sum_{m,m'}^{NN'} a_m \text{Re}[e^{iQ \cdot (r_m - R_m)}] \right\rangle \quad (3c)$$

$$S_{m+L+D}(Q) = S_{m+L}(Q) + c^2 P(Q) + c I(Q) \quad (3d)$$

$P(Q)$ can now be found from the difference equation;

$$F(Q) = \frac{S_{m+L+D}(Q) - S_{m+L}(Q)}{c} - \frac{S_{m+L+H}(Q) - S_{m+L}(Q)}{b} \quad (4)$$

And;

$$F(Q) = cP(Q) - I(Q) - bP(Q) + I(Q) = (c - b)P(Q)$$

With $P(Q)$ now known, $I(Q)$ can be calculated from either of equations (3b) or (3d). Notice that both $P(Q)$ and $I(Q)$ contain information on how hydrogen gathers near dislocations.

Hydrogen Cross Section Estimate

Here we estimate the magnitude of the hydrogen scattering cross section. We ignore the hydrogen-metal interference terms. We do assume however that the hydrogen does enter the metal either uniformly throughout, which we shall call bulk hydrogen, or associated with a dislocation. The

latter will appear as the additional hydrogen per unit length of dislocation line. The amount of additional hydrogen per unit length of dislocation, ΔC^L , will be calculated for a hydrogen annealed solubility of 5000 ppm in palladium with a dislocation density of $\rho_L = 2 \times 10^{11} \text{ cm}^{-2}$. The hydrogen solubility enhancement at 5000 ppm is given in Table 2 as 1.7. The following equation can be written for the deformed hydrogen concentration;

$$\begin{aligned} C^{\text{deformed}} &= C^{\text{bulk}} V^{\text{bulk}} + (C^{\text{bulk}} + C^L) V^L \\ C^{\text{deformed}} &= C^{\text{bulk}}(V^{\text{bulk}} + V^L) + C^L V^L \\ C^L &= (C^{\text{deformed}} - C^{\text{bulk}})/V^L \\ \Delta C^L &= C^L(V^L/\rho_L) = (C^{\text{deformed}} - C^{\text{bulk}}) 1/\rho_L \end{aligned}$$

And $V^{\text{bulk}} = 1 - V^L$, where V^L is the volume fraction of dislocations containing additional hydrogen atoms. At 5000 ppm hydrogen in Pd;

$$\begin{aligned} C^{\text{deformed}} &= 8500 \text{ ppm} = 5.95 \times 10^{20} \text{ H atoms/cm}^3 \\ C^{\text{bulk}} &= 5000 \text{ ppm} = 3.5 \times 10^{20} \text{ H atoms/cm}^3 \\ \Delta C^L &\sim 12 \text{ H atoms} / \text{\AA} \perp \text{ length} \end{aligned}$$

The hydrogen cross section will be calculated for the specific dislocation geometry where the sample is oriented so that the dislocation line is perpendicular to Q . In this calculation, the value of ΔC^L from above is used along with a dislocation density of $\rho_L = 2 \times 10^{11} \text{ cm}^{-2}$ and an average dislocation length of 300 Å. Going back to equations (2) to include incoherent scattering, the dot product in the third RHS term is zero if the additional hydrogen atoms are assumed to lie close to the dislocation line. We now make the point that the additional hydrogen associated with the dislocations gives rise to enhanced scattering in the forward direction. The bulk hydrogen not associated with dislocations does not scatter coherently at low Q . The incoherent hydrogen scattering cross section and the coherent hydrogen scattering cross section are now written as;

$$\frac{N' \sigma_{\text{in}}^{\text{H}}}{4\pi} + \frac{\sigma_{\text{coh}}^{\text{H}}}{4\pi} \left\langle \sum_{m,m'} e^{iQ \cdot (r_m - r_{m'})} \right\rangle = \frac{N' \sigma_{\text{in}}^{\text{H}}}{4\pi} + \frac{\sigma_{\text{coh}}^{\text{H}}}{4\pi} (N'' - 1) N'' \quad (5)$$

where; $N'' \equiv (12 \text{ H atoms} / \text{\AA} \perp \text{ length}) \times 300 \text{ \AA} \perp \text{ length} = 3600 \text{ H atoms} / \perp$

The macroscopic scattering cross sections per steradian are;

$$\Sigma_{\text{in}}^{\text{H}} = \frac{N'' \sigma_{\text{in}}^{\text{H}}}{4\pi} \frac{1's}{\text{unit vol.}} + C^{\text{bulk}} N^{\text{Pd}} \frac{\sigma_{\text{in}}^{\text{H}}}{4\pi} \quad (6)$$

$$\Sigma_{\text{coh}}^{\text{H}} = (N'')^2 \frac{\sigma_{\text{coh}}^{\text{H}}}{4\pi} \frac{1's}{\text{unit vol.}} \quad (7)$$

We have evaluated the above hydrogen scattering cross sections as follows;

$$\Sigma_{\text{coh}}^{\text{H}} = [(N'')^2 \times 2 \times 10^{11} \text{ 1's} / (1\text{cm}^2 \text{ } 300 \times 10^{-8} \text{ cm})] \times 2 \times 10^{-24} \text{ cm}^2 / 4\pi \approx 0.14 \text{ cm}^{-1} \text{ sr}^{-1}$$

$$\Sigma_{\text{in}}^{\text{H}} = [(N'') \times 2 \times 10^{11} \text{ 1's} / (1\text{cm}^2 \text{ } 300 \times 10^{-8} \text{ cm})] \times 80 \times 10^{-24} \text{ cm}^2 / 4\pi +$$

$$+ [(5000 \times 10^{-6} \text{ H atoms / metal atom}) (7 \times 10^{22} \text{ metal atoms / cm}^3)] \times 80 \times 10^{-24} \text{ cm}^2 / 4\pi$$

$$\Sigma_{\text{in}}^{\text{H}} \approx 3.8 \times 10^{-3} \text{ cm}^{-1} \text{ sr}^{-1}$$

For comparison, the scattering cross section at $|Q| = 0.005 \text{ \AA}^{-1}$ from deformed Cu (Taglauer, 1968, Fig. 3) is given below;

$$\Sigma_{\text{Cu,1}}^{\text{Taglauer}} = 10 \times 10^{-24} \text{ cm}^2 \text{ sr}^{-1} \times 8.49 \times 10^{22} \frac{\text{Cu atoms}}{\text{cm}^3} = 0.8 \text{ cm}^{-1} \text{ sr}^{-1}$$

The coherent hydrogen scattering cross section calculation above represents the maximum scattering for $|Q| = 0$. The calculation illustrates two points; the incoherent hydrogen scattering (or incoherent deuterium scattering) is negligible, and the coherent scattering from hydrogen (or deuterium) appears to be large enough to be measured over the background. A calculation of $I(Q)$ was not attempted, but $I(Q)$ is expected to be of the same order as $P(Q)$, depending on the hydrogen-dislocation correlations.

A second estimate of the hydrogen cross section can be made by comparison with the known coherent response from polymer samples as measured, for example, at ORNL. Usable coherent signals at $|Q| \approx 0.01 \text{ \AA}^{-1}$ can be made for a 7.0 meter flight path, on a 1.0% deuterated, 99% protonated, sample of polystyrene of dimensions 1.0 cm diameter x 0.1 cm thick. The deuterons will be "strung out" on random polymer chains not unlike the deuterons correlated with a dislocation network. The total number of deuterons in such a polystyrene sample is 6×10^{19} per sample. To compare this with the deuterated metal, we assume a dislocation density of $2 \times 10^{11} \text{ cm}^{-2}$ and, according to the above discussion we may expect about 10 deuterons attached to the dislocation per $\text{\AA}$ of dislocation length. For a sample 1 cm in diameter and 0.4 cm thick, the number of deuterons per sample is 6.3×10^{19} .

That is, the deuteron densities are essentially equal. Based on this, we again expect to observe dissolved hydrogen signals over the deformed metal background.

Preliminary Results and Conclusion

Figure 1 shows the relative macroscopic neutron scattering cross section per steradian vs. Q from two 99.999% pure single crystal Cu samples, one undeformed and one compressed to 55% deformation as defined in Table 2. Figure 2 shows the net macroscopic cross section per steradian (net cross section defined as deformed sample cross section - undeformed sample cross section) as a function of $1/Q^3$. These measurements, made on the small angle diffraction machine at ANL, demonstrate our ability to observe SANS from moderately deformed single crystal Cu.

We believe the hydrogen cross section estimates presented above, together with experimental evidence of hydrogen-dislocation correlations and measurable signals from deformed Cu, justifies a SANS experiment designed to measure hydrogen-dislocation correlations. We hope to perform such an experiment at ANL soon.

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Figure 1. Relative macroscopic neutron scattering cross section per steradian vs. Q from two 99.999% pure single crystal copper samples, one undeformed and one compressed to 55% deformation as defined in Table 2.

Figure 2. Net relative macroscopic neutron scattering cross section per steradian (net cross section defined as deformed sample cross section - undeformed sample cross section) vs $1/Q^3$.

$S(Q)$ [Arbitrary Units]

Figure 1

Figure 2

Table 1
SANS From Deformed Copper

Authors	Material	Q range [$\text{\AA}^{-1}$]	Dislocation Density [cm^{-2}]
Epperson et al (1976)	Single Crystal Cu	$0.0026 \leq Q \leq 0.008^{[1]}$	3.1×10^{11}
Taglauer (1968)	Polycrystalline Cu	$0.004 \leq Q \leq 0.018$	$1-3 \times 10^{11}$
Christ (1964)	Polycrystalline Cu	$0.0055 \leq Q \leq 0.034$	8×10^{11}

[1] This Q range was obtained from Fig. 4 of Epperson et al (Epperson et al 1976), with $|Q| = 2h$.

Table 2
Measured Hydrogen Solubility Enhancements In Palladium

Authors	$\perp$ Density	Annealed Solubility	Solubility Enhancement ($\perp$ Sol. / Annealed Sol.)	Temperature
Flanagan et al (1976)	$\sim 2 \times 10^{11} \text{ cm}^{-2}$	1×10^{-3} at fraction	1.8	298 K
Flanagan et al (1976)	$\sim 2 \times 10^{11} \text{ cm}^{-2}$	5×10^{-3} at fraction	1.7	298 K
Flanagan et al (1982)	78% deformation [1]	1×10^{-3} at fraction	1.6	273 K
Kirchheim (1981)	73% deformation [1]	1×10^{-3} at fraction	~ 1.3	295 K

[1] % def = $(d_0 - d) 100/d_0$ where d_0 and d are sample thicknesses before and after deformation, respectively. No dislocation densities where given.

Note: $\perp$ denotes dislocation.