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The use of small angle neutron scattering in the study of hydrogen trapping at defects in metals

D.K. Ross*, K. Stefanopoulos¹, M. Kemali

Joule Laboratory, University of Salford, Salford M5 4WT, UK

Abstract

Small angle neutron scattering (SANS) techniques have been used to investigate the trapping of hydrogen and deuterium on dislocations in palladium. Calculations of the expected form of this scattering are presented. It is shown that the different scattering lengths of H and D, respectively negative and positive, can be exploited to prove explicitly that the hydrogen is being trapped at the feature that is causing the SANS in the metal sample. In particular, at an edge dislocation, we can expect the H/D to be trapped in the region of lattice dilation below the edge. Thus, because the scattering length of palladium is positive, deuterium trapping will compensate for the reduction in the scattering density in the host lattice and hence will reduce the intensity of the SANS progressively as D is added, until the local scattering density deviation becomes positive. At this point, the overall SANS cross-section passes through a minimum. On the other hand, increasing H trapping will continuously increase the SANS intensity. The model for the expected scattering is described and measurements of the SANS intensities from dislocations in palladium are presented for a series of D concentrations. A minimum is observed in the SANS at about 1% atomic concentration, in reasonable agreement with the theory. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Small angle scattering, whether X-ray (SAXS) or neutron (SANS), provides a powerful way of examining defects in lattices because the signal is only sensitive to deviations from the scattering density of the perfect lattice and so the technique is capable of measuring quite small concentrations of defects. Moreover, these deviations can be observed on a length scale that is large compared to the lattice parameter. The technique essentially measures the Fourier transform of the departure of the respective scattering density from the average value for the lattice — multiplied by its complex conjugate and averaged over all the defects in the lattice. Thus, although the result is less easy to interpret than a direct image, for many purposes, the measured average value is more useful. The scattering density for X-rays is proportional to the electron density and this increases monotonically with Z . In contrast, neutrons measure the density of the neutron–nucleus scattering length, which varies from isotope to isotope. It is

also sensitive to the density of unpaired electrons and can therefore also measure magnetic defects. It is particularly sensitive to hydrogen, an element that is notoriously difficult to locate by conventional means and here we have the additional advantage that there are two isotopes, H and D, that are relatively easily available and which have scattering lengths of different sign. This difference is particularly useful in that we are often interested in determining where the hydrogen is trapped in the solid, i.e. with which kind of lattice defect it is associated. Thus, the neutron waves being scattered from different parts of the same defect will interfere with each other, whether they are scattered from the original defect or from the hydrogen trapped at the defect. The identification of the trapping defect can thus be made unambiguous by comparing measurements made with both isotopes.

In the present paper, we report on the use of this technique to investigate the trapping of hydrogen and deuterium in the vicinity of dislocations in palladium. We have chosen to use palladium as the host lattice because it is easy to control the amount of hydrogen absorbed and because the amount of hydrogen trapped on dislocations in this system has already been studied in some detail [1]. We first summarise the model we have developed to describe

*Corresponding author.

¹Present address: MESL, NCSR “Democratos” Institute of Physical Chemistry, 15310, Aghia Paraskevi, Athens, Greece.

the SANS from an edge dislocation both bare and with trapped H (D). Details of this treatment can be found elsewhere [2]. We then describe some recent experimental data which indicate that the SANS cross-section does pass through a minimum as the deuterium content is increased, as predicted by our model.

2. Theory

The SANS from a set of defects in a lattice is given by the expression

$$d\Sigma/d\Omega = N_d \left\langle \left| \int_V \Delta\rho \exp(i\mathbf{Q}\cdot\mathbf{R}) dV \right|^2 \right\rangle$$

where $d\Sigma/d\Omega$ is the macroscopic angular cross-section and where $\rho(\mathbf{r})$, the scattering density at position \mathbf{r} , is given by

$$\Sigma_i b_i(\mathbf{R}_i) = \rho(\mathbf{r}) \Delta V$$

and $\Delta\rho(r)$ is the deviator from the average value. Here, i is taken over all the atoms, position \mathbf{R}_i and scattering amplitude, b_i , in the volume ΔV of the defect and \mathbf{Q} ($=\mathbf{k}' - \mathbf{k}_0$) is the wave vector transfer in the scattering event. The averaging $\langle \rangle$ is taken over all the N_d defects where we are able to sum the intensities because we assume the defects to be uncorrelated in space.

The interpretation of SANS data inevitably involves the development of a suitable model. The first model for SAS from dislocations was given by Atkinson and Hirsch [3,4]. These authors determined the density change from the continuum expressions for the strain field surrounding an edge dislocation (screw dislocations do not generate long-range strain fields and so do not give rise to significant SANS). They considered dislocations having straight segments of length H and the dislocation strain field was assumed to cut off at a distance, R , about half the distance to the nearest dislocations of opposite sign. They showed that the SANS would vary as Q^{-3} with a tail at large Q that varies as Q^{-1} due to the core of the dislocations, a contribution that cannot be properly described by continuum theory.

Theories for the distribution of H(D) trapped round an edge dislocation have been developed by a number of authors, for example Kirchheim [5]. The chemical potential of a trapped atom, relative to a site in the perfect lattice, $\Delta\mu_H$, is given by

$$\Delta\mu_H = -\sigma_h V_H$$

Here, σ_h is the local tensile stress and V_H is the partial molar volume/hydrogen atom. Now, the site occupation probability has to be described by the Fermi–Dirac distribution because there can only be one H on a given site. We can now equate the chemical potential in the perfect lattice to the chemical potential at any point r, θ relative to

the dislocation. The major deficiency with this logic is that it does not allow for the expansion of the lattice caused by adding a hydrogen atom to a site that has been dilated by an amount less than V_H . In this case, the surrounding lattice atoms would have to relax back from the trapped atom and would therefore provide smaller trapping energies in their vicinities. To account for this effect, we have introduced an ansatz that will allow for the effect to a first approximation. The assumption is that the local trapping energy is scaled by the local trapped density in such a way that it goes to zero when the total volume of the trapped H atoms per unit volume equals the total volume dilation due to the tensile stress per unit volume. This assumption produces an intrinsic equation that can be solved for the trapped concentration, $c(r, \theta)$. From $c(r, \theta)$ and the expression for the lattice dilation, we obtain the expression for the change in the overall scattering density, $\Delta\rho(r, \theta)$. In Fig. 1 we show the variation of $\Delta\rho(r, \theta)$ with distance from the dislocation core at a fixed angle, $\theta = 90^\circ$, being the direction in which the strain and the trapping are both a maximum. In the left graph, (a), we show calculations for hydrogen, and in the right, (b), calculations for deuterium. In both cases, the inverted triangles refer to the effect of the strain in the palladium, which is negative because the scattering length of palladium is positive. In Fig. 1a we show the effect of adding the scattering density due to the trapped hydrogen (in equilibrium with a concentration of H of 0.5 and 3% in the undistorted lattice). It is clear that adding hydrogen will always increase the deviation of the scattering density from the value for a perfect lattice. The data shown are calculated both using the expression for trapping in the fully relaxed lattice — using the ansatz above — and for no relaxation. The relaxation, of course, reduces the extent of the trapping. In Fig. 1b, we show the equivalent curves for trapping deuterium (2 and 3% in the undistorted lattice) along with the bare palladium curve. Here, of course, the deuterium contribution is positive and the resulting scattering density change is much reduced, except near the core where the contribution from the trapped deuterium predominates. Clearly, a concentration of 1–2% corresponds to the minimum in the resulting scattering cross-section. With less deuterium, the palladium will have more of its original effect. With more deuterium, the scattering density will become increasingly positive and the cross-section will increase correspondingly.

The next stage is the calculation of the actual scattering cross-section. While Atkinson and Hirsch [3,4] were able to do this analytically, we obviously have to do it numerically because of the complex H,D trapping expressions. The results are shown in Fig. 2. Again, the left part, (a), is for hydrogen, and the right part, (b), is for deuterium. In both, we show the cross-section for the bare palladium, which has a gradient of about Q^{-3} at higher Q but bends over somewhat at lower Q , due to the assumed length of the dislocation segment (dislocation density). As expected, for deuterium, the 0.5% D case is lower than the

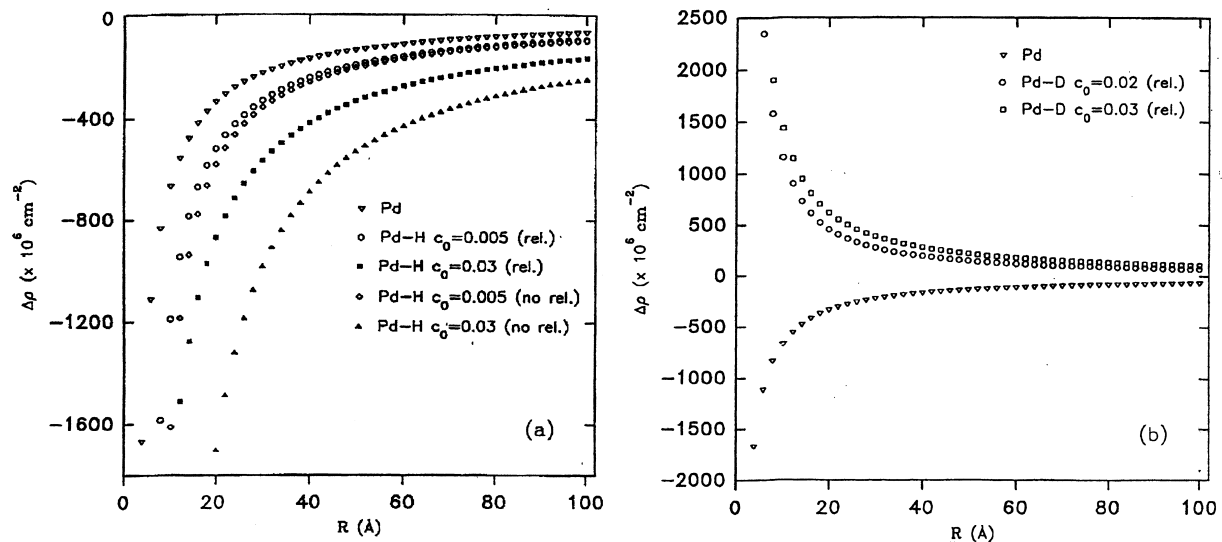


Fig. 1. The departure of the neutron scattering density from the value for the undeformed lattice for (a) H trapping and (b) D trapping. The data for palladium alone is shown in both diagrams. In (a), we also show the total change in scattering density for 0.5 and 3% H for both the unrelaxed and the relaxed models. In (b), we show the relaxed data for 2 and 3% D concentration for the relaxed calculation.

bare Pd, while the 3% D case is higher (both relaxed and unrelaxed).

3. Experimental details

Our measurements were made on both the LOQ instrument at ISIS (Rutherford Appleton Laboratory, UK) and the D11 instrument at the ILL (Grenoble, France). The palladium foils of 0.1 mm thickness were purchased from Aldrich Chemicals Ltd. with a nominal purity of 99.995%.

On receipt, they were outgassed in a vacuum of 10^{-6} mbar at a temperature of 900°C for 2 days to remove any existing dislocations. The foil surface was subsequently activated by briefly exposing it to air at red heat. The amount of oxidation produced was kept to an absolute limit because it was found that the palladium black produced could itself generate SANS. Initially, the dislocations in the samples were produced by unidirectional rolling but this method had to be abandoned because it was found that the dislocations tended to anneal out while the hydrogen was being inserted, even at room temperature.

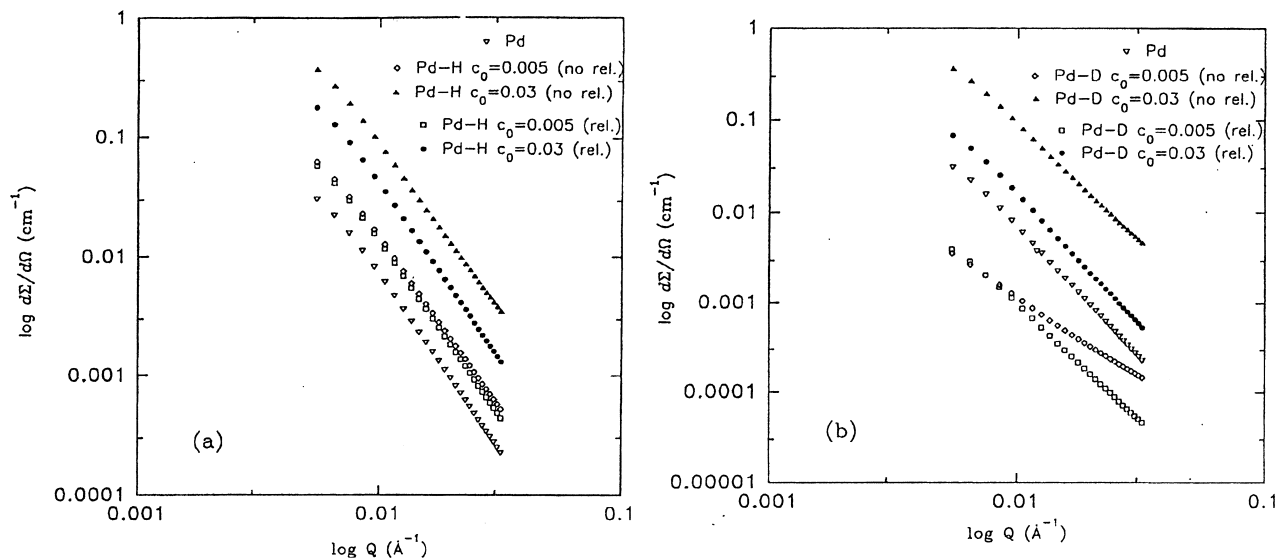


Fig. 2. Calculated cross-sections for H and D trapping on edge dislocations. The upper graph shows the prediction of the model described in the text for Pd and for 0.5 and 3% H for both the relaxed and the unrelaxed calculation. The lower graph shows equivalent data for D. It should be noted that the unrelaxed data for 0.5% D deviates from the other cases because the two contributions to the scattering density most nearly match in this case. The remaining scattering density is at the core of the dislocation so one expects Q^{-1} dependence.

Similarly, although it was found that passing through the alpha–beta transition produced a stable set of dislocations, this method suffered from the problem that it was subsequently difficult to remove all the hydrogen from the foils without heating them — which would have annealed out the dislocations. On the other hand, if hydrogen or deuterium were left in the sample, it would have invalidated any quantification of the total hydrogen (deuterium) content when more gas was added by use of a calibrated volume. For this reason, we eventually decided to produce the dislocations by cross-rolling. We believe that this process gave rise to a stable dislocation network. A further problem is that the as-received foil after vacuum annealing shows a Q^{-4} scattering component. Attempts to recycle the foil after work hardening caused this scattering to increase considerably. It could be removed by melting the palladium but it is impossible to re-cast into a convenient sample shape. TEM images confirmed our suspicion that this scattering was due to small voids, presumably generated by the coalescence of vacancies produced by the interaction of dislocations with each other. While, in principle, SANS from this source will be uncorrelated with that from the H(D) trapped on dislocations and it can therefore be subtracted off, there is always the possibility that it also will be altered by the addition of H(D). It was therefore important to keep this contribution to a minimum.

During the runs on LOQ, the deuterium was added and

subsequently removed to yield concentrations down to 1.4%. A final point quoted as $>1\%$ was produced by pumping on the foils for over 36 h. For the D11 sample, D was added from a calibrated volume, starting from zero D concentration. After the usual inter-normalisation procedures, the background and scattering from the as-received sample were subtracted. The data from LOQ are shown in Fig. 3. As can be seen, the curves are all more or less parallel. As expected, the intensities of the signal initially decreased with reducing D content, down to 1.4% D and 1% D, which have about the same intensities. The final sample, where pumping on the sample ensured that the D content was less than 1%, was clearly above the former two curves. The intensities taken at a Q of 0.01 \AA^{-1} are plotted in Fig. 4 as a function of concentration along with three values taken for the same Q value from the subsequent D11 run at the ILL. It should be appreciated that complete matching of intensity would not be expected as the dislocations were introduced separately to the samples. The results are certainly consistent with there being a minimum in the intensity at a concentration of about 1% D. It will also be noted that all the LOQ curves show a change of gradient at about 0.2 \AA^{-1} . On the lower Q side, the gradient is around -3.4 , while on the high Q side they are around -2.2 . The former gradient ought to correspond with the calculation but is somewhat higher. The change to the lower gradient is also expected as the scattering will be dominated by the scattering from the core. It will thus be

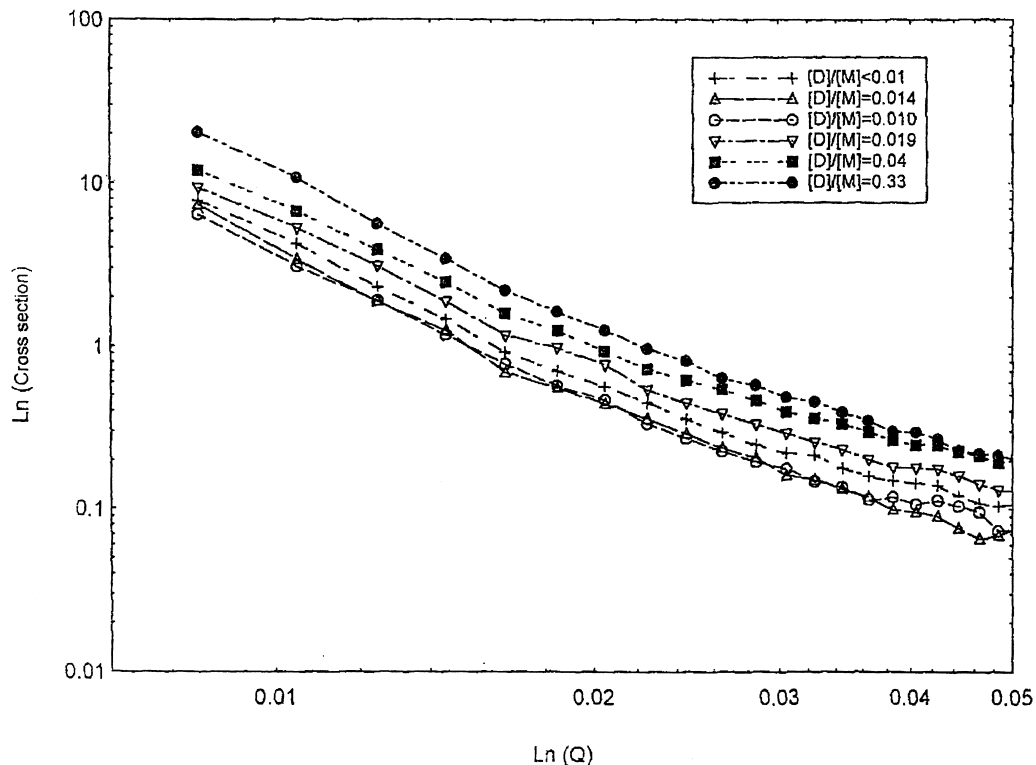


Fig. 3. SANS data obtained with the LOQ spectrometer for a series of concentrations obtained by progressively removing measured amounts of D from the sample.

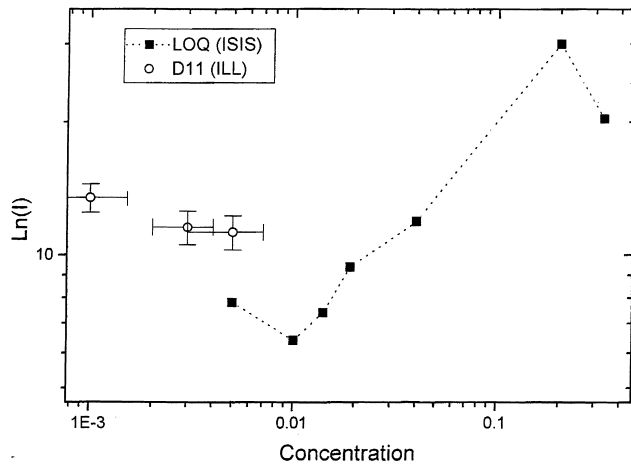


Fig. 4. Variation of the SANS intensity measured at $Q = 0.1 \text{ \AA}^{-1}$ for both the LOQ and D11 cases.

seen that the present results can be explained on the basis of the calculations outlined above. A fuller analysis of the results can be found elsewhere [6].

4. Conclusion

Measurements of the SANS from D trapped on dislocations have confirmed our calculations which predict a

minimum in the scattering intensity at a concentration of about 1% D. The observation of a minimum confirms that the deuterium is trapped at the dislocation. Our model predicts the Q dependence of the scattering at low Q , with the expected deviation at higher Q due to the core of the dislocation. We believe that the method described here can be used to determine the trapping of D at other types of defect.

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