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THE INFLUENCE OF N-IMPURITIES ON THE DIFFUSION COEFFICIENT OF H AND D IN Nb AND Ta

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Abstract.— Gorsky-effect measurements of the diffusion coefficient of H and D in Nb and Ta in the presence of N interstitials are reported. The influence of the N interstitials on the diffusion coefficient is correlated with the low-temperature diffusion anomaly of H in the pure metals. For H in pure Nb and pure Ta the activation enthalpy decreases strongly below about 250 K which suggests a change of the microscopic diffusion mechanism. For these two systems the reduction of the diffusion coefficient due to N interstitials is particularly effective in the region of the low activation enthalpy leading to a suppression of the low-temperature diffusion process at the largest N concentrations. On the other hand, for D in Nb and Ta for which no decrease of the activation enthalpy is observed in the pure metals only a minor reduction of the low-temperature diffusivity by the N interstitials is found. The results cannot solely be explained by trapping effects. The low-temperature diffusion mechanism is particularly strongly influenced by the N impurities.

1. Introduction.— Interstitial impurity atoms modify the behavior of metal-hydrogen systems /1-19/. The most direct effect is trapping, which is commonly used as explanation for many experimental results. Such results are deviations from Sievert's law /1-4/, changes in the phase diagram /5-8/ and especially in the solubility limit of the α-phase, resistivity differences between trapped and free H /5,6/, and elastic relaxation effects caused by trapped H /9-14/. Recently, also the tunneling of trapped H was observed in low-temperature specific heat /15/ and neutron-scattering /16/ measurements. In this study the influence of N interstitials on the diffusion coefficient of H and D in Nb and Ta is investigated. The experiments are a continuation of a previous work of Münzing et al. /17/ which was confined to the system Nb-N-H. For Nb the influence of interstitial impurities on H diffusion was also studied by Matusiewicz et al. /18/ and by Richter and Springer /19/.

2. Experimental.— Our experiments were Gorsky-effect measurements /20-22/ on Nb or Ta foils of 0.25 or 0.1 mm thickness. The foils were purified by annealing at temperatures close to the melting point in a vacuum of several 10^{-10} mbar. The resistivity ratio of samples measured after this annealing was better than 1000, which indicates that the

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content of residual N, O, or C impurities was less than 30 at-ppm. For N doping, the samples were exposed to appropriate N₂-gas pressures at about 2000 K /23/ (immediately after the purification procedure). The exact N-concentrations achieved were determined from the residual resistivity ratios. The samples were loaded with H or D electrolytically, and in some cases also from the H₂-gas phase.

2. Results.- The results for the diffusion coefficients are compiled in Figs. 1 to 4. In both metals, Nb and Ta, the presence of N impurities reduces the diffusivity of H and D. The reduction is the more pronounced the lower the temperature.

For H in both Nb and Ta, the diffusion coefficient is especially strongly reduced below ~250 K, where a decrease of the activation enthalpy is observed in the pure metals. This low-temperature anomaly, which is yet theoretically unexplained, is an indication for a change of the predominant microscopic diffusion mechanism. The particularly large influence of the N below ~250 K leads, at the largest N-concentration, to a complete suppression of the low-temperature diffusion mechanism; the temperature dependence of the data can now be described by a single activation enthalpy over the whole temperature range of the measurements.

Contrary to the results for H, the diffusion of D in pure Nb and Ta* does not show a low-temperature anomaly so that the data can be described by a single activation enthalpy. This behavior is also observed for the N-doped samples, for which the value of the activation enthalpy becomes slightly larger with increasing N concentration.

A remarkable result of our data is that the change in the diffusion coefficient due to N doping is independent of the H or D concentration. This behavior is particularly well demonstrated by the results for D in Nb (Fig. 3) where, for samples with 0.26 at% N, the D concentrations vary by a factor of almost 8 from 0.11 up to 0.82 at% without noticeable changes in the diffusivity.

Discussion.- Diffusion in the presence of impurities is frequently discussed within trap models like that of Oriani /25/. In this model, it

* A previously reported experiment /22/ showing a low temperature decrease of the activation enthalpy also for D diffusion in Ta was spoiled by the accidental presence of several 100 at-ppm H as a consequence of a recrystallisation process which was applied in order to remove cold-work dislocations. Since the D concentration was of the same order of magnitude the slow Gorsky relaxation due to D remained hidden behind the fast Gorsky relaxation of H. (In the present experiments such a recrystallisation was not necessary).
Fig. 1 Diffusion coefficient of H in undoped and N-doped Nb /17/

Fig. 2 Diffusion coefficient of H in undoped and N-doped Ta. The figure includes also previous results of Rückel /24/
Fig. 3 Diffusion coefficient of D in undoped and N-doped Nb

Fig. 4 Diffusion coefficient of D in undoped and N-doped Ta
is assumed that (i) trapped H is eliminated from the diffusion process, and (ii) the H diffusivity between traps remains unchanged. The diffusion in the presence of traps can then be described by an effective diffusion coefficient $D_{\text{eff}}$ given by

$$D_{\text{eff}} = D \cdot \frac{\partial c_{\text{free}}}{\partial c_{\text{tot}}}$$

In this equation, $D$ is the diffusion coefficient measured in the absence of traps. The differential quotient describes how much — under equilibrium conditions — the concentration $c_{\text{free}}$ of free, untrapped H increases for a differentially small increase of the total H concentration $c_{\text{tot}}$.

In agreement with the predictions of this theory, the experimental diffusion coefficient $D_{\text{eff}}$ is indeed smaller than or at least equal to the diffusion coefficient $D$ in the absence of traps. However, it is not possible to achieve a quantitative description of our data by the trapping model, except by considering a multiplicity of trap sites. The main reason for this is that the data show, for a given N content, no dependence on the H(D) concentration, whereas in the trap model such a dependence is predicted for our experimental range of H(D) and N concentrations. Further, within the trap model, it must be considered to happen purely fortuitously that in both Nb and Ta N impurity atoms suppress so effectively the low-temperature diffusion mechanism of H. The model leads finally to a convex curvature of the diffusion coefficient in an Arrhenius plot (larger activation enthalpies at lower temperatures), a behavior certainly not substantiated by the present data. (Especially for D a convex curvature is expected since no low-temperature anomaly is observed in pure Nb and Ta).

We conclude that the trapping model discussed above solely cannot quantitatively explain all the features of H(D) diffusion in the presence of impurity atoms. A likely reason for this failure is changes in the bulk diffusivity also between the impurity atoms, caused for instance by far-reaching lattice strains around these impurities. Our results show that the low-temperature diffusion mechanism (observed for H but not for D) is particularly effectively suppressed by impurities.

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