NOTIZEN

Reversed Isotope Dependence for Hydrogen Diffusion in Palladium

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Herrn Prof. Dr. N. Riehl, der wesentliche Beiträge
zur Protonendiffusion im Eis geleistet hat,
zum 70. Geburtstag gewidmet

Gorsky-effect measurements applied to H and D in Pd show that D diffuses faster than H in the temperature range from about −60 °C to 200 °C. The diagonal components of the dipolemoment tensor has been estimated as 3.5 eV.

Classical rate theory predicts[1, 2] that light isotopes diffuse faster than the heavier ones. This prediction is quite generally observed for heavy isotopes. Also for light isotopes like H and D in V, Nb and Ta this prediction is valid, although classical rate theory can not explain the experimental data otherwise[3]. In contrast to these observations Bomholdt and Wicke[4] and Holleck and Wicke[5] report diffusion measurements of H and D in Palladium which show the reversed isotope dependence. It therefore was of particular interest to apply the recently developped method for diffusion measurements, based on the Gorsky effect[3, 6], to Pd.

The samples were coiled polycrystalline springs with wire diameter 0.5 mm. They were copperplated in order to slow down the hydrogen loss, subsequently outgassed at 450 °C and charged by exposure to clean hydrogen gas. The concentrations ranged from 0.2 to 0.6 atom-%. More experimental details are given in Ref.[3].

The results are plotted in Fig. 1 showing the reversed isotope dependence for the temperature range investigated. The diffusion coefficients can be represented by the relations

$$D_{\mathrm{H}} = (2.5 \pm 0.5) \cdot 10^{-3} \exp[-(0.226 \pm 0.006)\,/k\,T]$$
$$D_{\mathrm{D}} = (1.7 \pm 0.6) \cdot 10^{-3} \exp[-(0.206 \pm 0.007)\,/k\,T]$$

where D is measured in cm²/sec and $k\,T$ in eV.

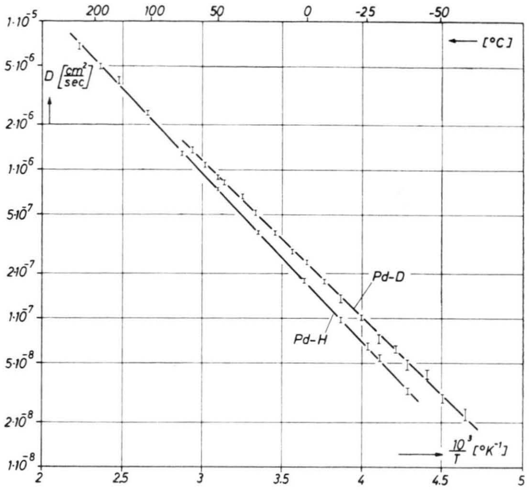

Fig. 1. Logarithm of the diffusion coefficient of H and D in Pd as a function of the reciprocal temperature.

The diffusion coefficient for hydrogen agrees very well with that determined by Holleck[7] at higher temperatures (245 °C − 615 °C) by means of a permeation method. In this reference and Ref.[7a] a collection of data of other authors is given. Qualitatively the data of Bomholdt and Wicke[4] and Holleck and Wicke[5] agree with ours, although differences can be noted in the absolute values of the preexponential factor D_0 and the activation energy U.

The ratio of the preexponential factors is within the errors given by the classical value $\sqrt{2}$, thus leading to the common isotope dependence for $T \rightarrow \infty$. The reversed isotope dependence below 600 °K is caused by the observation that $U_{\mathrm{H}} > U_{\mathrm{D}}$. Assuming equally high activation barriers for both isotopes one would expect the opposite relation, since the zero point energy for D is lower than for H. Yet Jost and Widmann[8, 9] and Holleck and Wicke[5] have pointed out that this assumption may not be fulfilled, if, in a semiclassical picture, a zero point energy for the degree of freedom transverse to the reaction coordinate must be taken into account. Depending on the curvatures of the potentials

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in the equilibrium position and the saddle point both relations $U_H \gtrless U_D$ are possible. Similar ideas are explicitly or implicitly contained in semiclassic treatments by LE CLAIRE [10] and EBISUZAKI et al. [11, 12].

From the experimental value of the Gorsky relaxation strength $\Delta_E = 2\%/\text{at.-}\%$ H ($\pm 10\%$) at 298 °K the dipolemoment tensor $P_{ij} = P\,\delta_{ij}$ can be determined [13] if the proper value for the orientation dependent factor Ω is known [Eq. (19) in Ref. [13]]. For this, actually a complicated averaging procedure, taking into account the spectrum of grain orientation distributions would be required. Since the exact averaging procedure has not yet been worked out, we used $\Omega = 1.8$, which is the average between the two extreme values, yielding $P = 3.5$ eV. This value of the dipolemoment tensor may be compared with $P \approx 4$ eV, as calculated from the critical temperature of H in Pd [14].

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The Pyroelectric Effect in Lithium doped Cadmium Sulfide

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CdS crystals highly doped with Li, showing the tap-effect [1] have pyroelectric constants considerably higher than those reported by MINKUS[2] for pure CdS crystals. The differences of the surface charges during cooling and heating can be explained by considering the exponential temperature dependence of the electric conductivity of the crystals.

In 1968 PARK and LITTON [1] reportet that Li-doped CdS crystals, after cooling in darkness to the temperature of liquid nitrogen, emit flashes of light when tapped with a pointed metal object. They therefore called this phenomenon tap-effect. As preliminary experiments showed, the mechanical vibration caused by tapping is not a prerequisite for the emission of light. Even lightly touching certain surfaces of the crystal with the pointed metal object suffices. This results in an electric discharge followed by luminescence. It was assumed that the cooling leads to high surface charges. Therefore the pyroelectric properties of these Li-doped CdS crystals were investigated.

To measure the surface charge, the crystal is insulated by mica foil placed between the electrodes of a capacitor. One electrode is the copper block of the cryostat to be heated and cooled. The other electrode is made of quartz glass which is coated with a layer of transparent conductive SnO_2. The CdS crystals are so orientated that the planes which are orthogonal to the *c*-axis are parallel to the electrodes. The charge induced in the electrodes is measured with an electrometer (Keithley 610 C) and registered on a pen recorder. The charge measured by the electrometer as a function of the temperature when the crystal is in darkness is shown in Fig. 1. Cooling is represented by the continuous line, heating by the dotted line.

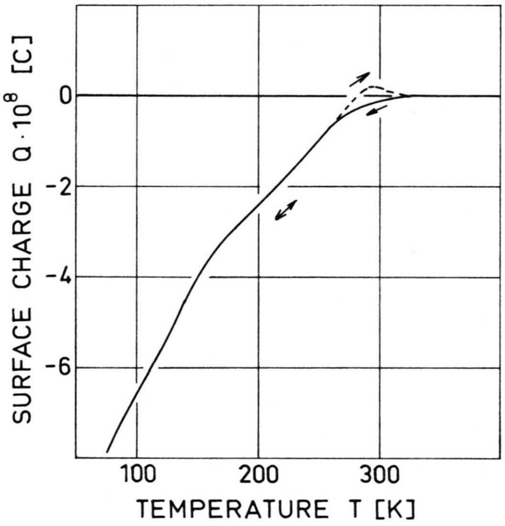

Fig. 1. Measured surface charge as a function of temperature, ——— cooling, – – – heating.

Above 320 K no charge is registered. Below 260 K the cooling curve is identical to the heating curve. In the intermediate range there are differences between both curves. It can be shown that the conductivity which increases exponentially with temperature is the reason for the difference. At temperatures rising above 260 K the conductivity leads during the time of measurement to a rapidly increasing compensation of the surface charge caused by the pyroelectric effect.

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