

Excitation of Hydrogen Motion inside a Nickel Vacancy

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By means of the ion-channeling technique, we have shown the existence of a very low-energy (~ 3 meV) excitation for deuterium impurities trapped to vacancies in nickel. The excitation is associated with a change of the D location from near octahedral to near tetrahedral. On the basis of calculations of the D potentials within the effective-medium theory and the quantum treatment of the D motion, we suggest that the observed state can be regarded as an excited standing wave of a particle (D) on a sphere (internal surface around the vacancy).

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The interaction of hydrogen isotopes¹ with defects in bulk metals has been the subject of an increasing number of detailed investigations (for reviews, see Besenbacher, Myers, and Nørskov² and Myers *et al.*³), and very recently, new insight into the microscopic nature of the hydrogen-metal interaction has been gained from an interplay between experiment and theory.^{4,5}

In the present Letter, we consider D trapped to vacancies in nickel and demonstrate the existence of a very low-energy (~ 3 meV) excitation which is characterized by a tetrahedral-like D-lattice location, as opposed to the near-octahedral site of D in the ground state in the vacancy. We propose that this excitation corresponds to the motion of D around the vacancy. The results offer a new interpretation for other metal-hydrogen systems such as, e.g., D trapped to vacancies in palladium.

The experimental setup and method have been previously detailed.⁶ The following is a brief description: D was implanted at 25 K into Ni single crystals along a random direction at an energy of 15 keV and at a fluence of 6×10^{14} D/cm². The total amount and the depth distribution of D were monitored by ion-beam analysis detecting either protons or α particles from the 750-keV ³He-excited nuclear reaction $D(^3\text{He}, p)\alpha$. The D-lattice location was determined by the ion-channeling technique.⁷ The crystals were subjected to isochronal-annealing sequences of 15 min at tempera-

tures ranging from 25 to 270 K and then cooled to the implant temperature of 25 K, at which the analysis, i.e., the lattice location, was performed. The detailed analysis of the channeling results was performed by comparison of the measured angular yields with theoretical multirow continuum-model calculations.

An increase in annealing temperature will cause a shift in occupancy from solution to weaker and finally stronger traps, and after an anneal at $T_a = 270$ K, D populates the strongest lattice-defect traps, i.e., vacancies exclusively.⁶ The corresponding D angular scan for the $\langle 100 \rangle$ axis is shown by the open circles in Fig. 1. We have not been able to find a unique site that explains these channeling data. To account for the experimental results given by the open circles in Fig. 1, we assumed, for simplicity, two positions only, and the lower dashed curves in Fig. 1 is calculated for 87% of the D displaced 0.3 Å from the octahedral (O_h) site towards the vacancy, and the remaining 13% displaced 0.2 Å from the tetrahedral (T_h) site towards the vacancy.

In Fig. 2, we show results of a calculation of the binding energy of D in a Ni vacancy using the effective-medium theory.⁸ Also shown are the D ground-state densities, i.e., the square of the atom ground-state wave function which is obtained by solving the Schrödinger equation for a D atom moving in the calculated potential.⁹ The D atom is clearly delocalized but with clear maxima between the vacancy

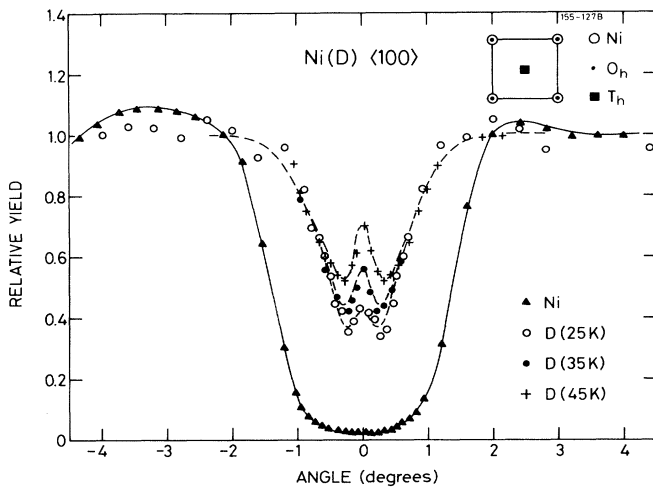


FIG. 1. Normalized channeling yields from D and Ni after annealing at $T_a = 270$ K for 15 min. The measurements are carried out at 25, 25, and 45 K, respectively, and are reversible with respect to temperature. In the top corner, the projection of the $\langle 100 \rangle$ channel is shown, and it is seen that displaced O_h and T_h sites are uniquely separable from a $\langle 100 \rangle$ axial scan since a T_h site is located in the center of the $\langle 100 \rangle$ axis, resulting in a flux peak, whereas the O_h site is shadowed by the Ni rows of atoms, resulting in a channeling dip that is narrowed for a displaced O_h site (Ref. 7). Channeling scans were carried out along other major axial and planar directions, and these results were consistent with the present $\langle 100 \rangle$ results.

and the O_h sites. Qualitatively, the maxima at displaced O_h sites and the delocalized nature of the ground-state D density is consistent with the experimental results. Quantitatively, however, the D density in the region between the vacancy and the T_h site is probably not sufficient to account for the 13% T_h -like occupancy. The maxima of the displaced O_h site is closer to the vacancy than the experimentally determined position by ~ 0.65 Å, corresponding to a difference in D-Ni bond length of about 0.2 Å. This reflects inaccuracies in the calculated potential.⁶

After the annealing to 270 K and the measurement at 25 K, we repeat this angular $\langle 100 \rangle$ scan but now with the measuring temperature increased to 35 and 45 K, respectively. The results are shown again in Fig. 1. It is seen that the T_h occupancy represented by the flux peak increases with temperature. This indicates that the T_h -like component must be an excited state which is increasingly populated with increasing temperature. These higher-temperature results were analyzed, once again with the assumption of only a displaced O_h and a displaced T_h site; the dashed curves through the experimental data are the results of such model calculations. The fraction of D in O_h - and T_h -like sites changes from (87%, 13%) at 25 K to (81%, 19%) at 45

K. When we plot the relative fraction of T_h occupancy in an Arrhenius plot (Fig. 3), a straight line is obtained, corresponding to an excitation energy of 3.3 meV.

In Fig. 2 we also include the calculated D density for the two low-energy excited states in the potential of Fig. 2(b). The calculated excitation energies of the two states are 4 and 14 meV, respectively, i.e., of the same order of magnitude as the experimental value. Deuterium density contours [Figs. 2(d) and 2(e)] are clearly seen to be more T_h -like than those for the ground state [Fig. 2(c)], once again in qualitative agreement with the experimental findings. It can be seen from Fig. 2(e) that the 14-meV state has more D density spread out in the central region of the $\langle 100 \rangle$ channeling axis than the 4-meV state, and thus this state will give a more pronounced flux peak for the $\langle 100 \rangle$ axial scan. The experimental results in Fig. 1 are thus most easily associated with the 14-meV excited state, even though the calculated excitation energy of this state is somewhat larger than that obtained experimentally. In this connection, the approximate nature of the calculated D potential should be kept in mind. It should also be pointed out that the coupling of the D motion to the lattice has not been included here.¹⁰

A very useful picture of the excitations discussed above can be obtained by consideration of the following analytically solvable model of the D motion in the vacancy. Assume that the D potential in Fig. 2(b) can be approximated by a spherically symmetrical potential $V(r)$. The wave function can then be written as $\psi_{nlm}(r) = [u_{nl}(r)/r] Y_{lm}(\theta, \phi)$, where Y_{lm} are spherical harmonics, and the radial wave function satisfies the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2Mr^2} + V(r) \right] u_{nl}(r) = \left[H_0 + \frac{l(l+1)\hbar^2}{2Mr^2} \right] u_{nl}(r) = E_{nl} u_{nl}(r).$$

We shall make the further assumption that the excitation energies of the Hamiltonian H_0 are large compared to $l(l+1)\hbar^2/2Mr^2$. This is well obeyed for small l for the potential in Fig. 2, where H_0 approximately describes a harmonic oscillator situated a distance R from the vacancy, with excitation energies $\hbar\omega_0 \sim 50$ meV, whereas $\hbar^2/2Mr^2 = 1.85$ meV. In this case, we can treat the centrifugal potential using first-order perturbation theory, and obtain the excitation spectrum which corresponds to the radial ground state, $E_{0l} = [\hbar^2/(2Mr^2)]l(l+1)$, where R is given by an expectation value of $1/r^2$. In the case of H_0 describing a harmonic oscillator, R is just the position of the minimum of the potential relative to the center of the vacancy. The only parameter determining the D exci-

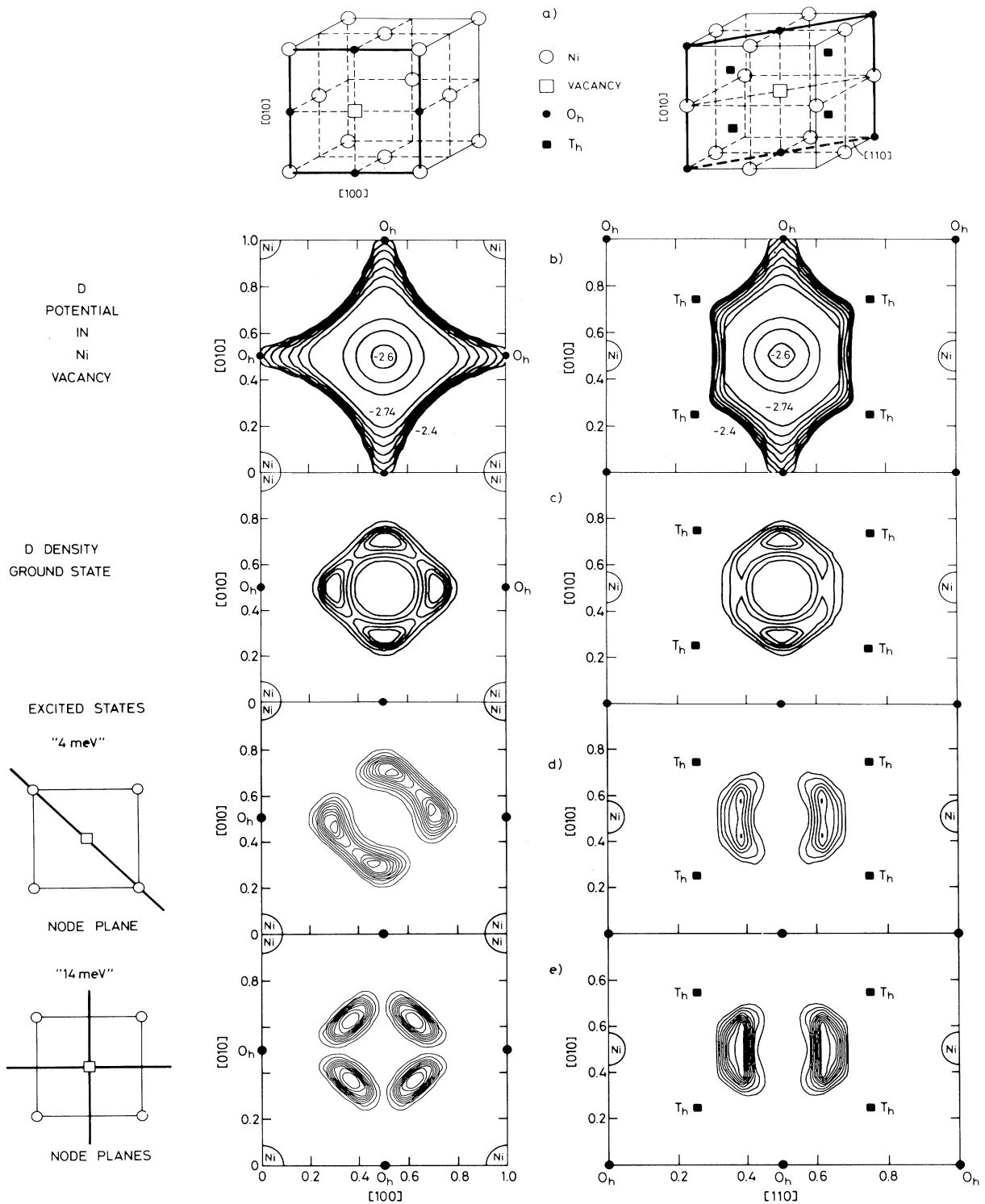


FIG. 2. Contour plots of the D potential (binding energy measured relative to a D atom at ∞) and D density (wave function squared) for D in a Ni vacancy for two different cuts (accentuated by thick solid line) through the center of the vacancy. The contour spacing is 0.05 eV in the potential plots and one sixth of the maximum in the density plots. From (a) it can be concluded that the projection of the $\langle 100 \rangle$ axis on the (100) plane is only one fourth of the accentuated $\langle 100 \rangle$ frame.

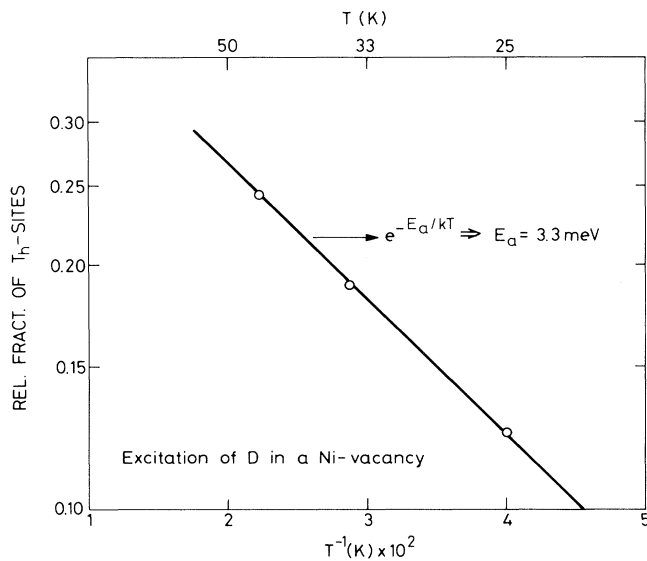


FIG. 3. The relative fraction of T_h occupancy as a function of $1/T(k)$.

tation spectrum is thus R , which can be read from Fig. 2. With $R=0.75 \text{ \AA}$, the $l=1$ and $l=2$ excitation energies are 3.7 and 11.0 meV, respectively, very close to the results of the numerical solution in the full potential. The excited states are just the p and d states (standing waves) of a particle (D) moving on a sphere. The p state has one mirror plane and the d state two, as indicated in Fig. 2.¹¹ Furthermore, if for R we use the experimentally determined value $R=1.4 \text{ \AA}$, we get excitation energies of 1.1 and 3.2 meV for the $l=1$ and $l=2$ states, and thus the energy of the $l=2$ state is in very good agreement with the experimental excitation energy.

We would expect the effects described above for Ni also to be present in other hydrogen-metal systems. In the simple model, the only parameter describing the system is R , which scales approximately with the lattice constant, and which furthermore can be determined experimentally. For Pd and Pt,¹² for example,

the larger lattice constant causes an increase in R and thereby a reduction of the excitation energies. This is in agreement with the experimental observations of a larger D fraction ($\sim 60\%$) in the delocalized T_h site ($l=2$) already at 25 K for these systems.

¹In the present Letter, we deal only with the hydrogen isotope deuterium.

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¹⁰Such effects can only be treated quantitatively in a dynamical treatment. Qualitatively, since the D excitation energy is lower than most phonon frequencies, the lattice will tend to follow the D motion. Such a situation can be described in terms of an increase in the effective mass of the impurity due to the drag of the metal atom (K. A. Muttalib and J. Sethna, to be published). The "static-lattice" excitation energy is therefore an upper bound on the real excitation energy.

¹¹In the full numerical calculation, the $l=2$ states split up into E_g and T_{2g} states. That which is shown in Fig. 2 is a T_{2g} state which is the one with most occupancy of the T_h sites.

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