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INTERACTION OF HYDROGEN ISOTOPES WITH METALS: DEUTERIUM TRAPPED AT LATTICE DEFECTS IN PALLADIUM

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ABSTRACT

From an interplay between theory based on the effective-medium scheme and experiments, an extremely simple picture has evolved which is capable of describing a vast number of experimental quantities related to interaction of hydrogen with metals, especially the trapping of hydrogen at defects. It is shown that the trap strengths are determined mainly by the interstitial electron density, and any open structures in the lattice leads to a trap, with the vacancies and voids being the strongest traps. It is also found theoretically and experimentally that up to six hydrogen atoms can be accomodated in a vacancy, and the change in trap strengths with occupancy has been determined. Recent results for the trapping of deuterium to defects in Pd are discussed.

Among all the metal-hydrogen systems, the hydrogen-palladium system is one of the most thoroughly studied[1-3]. This is due to several characteristics of the interaction of hydrogen isotopes with fcc palladium (Pd), including the high solubility and mobility, and also to the widespread use of Pd in hydrogen technology. Despite this broad and continuous interest in the palladium-hydrogen system, only limited information on the binding of hydrogen to defects and impurities in Pd is available at present.

The very recent suggestion of cold fusion of D atoms in Pd[4,5] has accentuated the interest in the interaction of deuterium (D) with defects in Pd. Vacancy-type defects are present in cold-worked samples and will in addition be created by the reaction products from a D+D-fusion reaction. The presence of vacancies changes the mobility of the D significantly, and furthermore, vacancies may be the nucleation sites for the creation of a high local concentration of D in Pd.

The present study is part of a continuing effort in which, a more general and quantitative understanding of the interaction of hydrogen isotopes with defects in metals is pursued (see Refs. 6-9). We have applied ion implantation and nuclear reaction analysis to study the trapping of deuterium (D) by lattice defects (e.g., vacancies) and by helium bubbles/voids in Pd. The experimental binding enthalpies and the corresponding equilibrium positions for D trapped at vacancies and at bubbles are compared with theoretical calculations based on the effective-medium scheme[6,7,10-11]. For the systems studied so far, Fe (Ref. 12-14), Ni (Ref. 15-19), Cu (Ref. 20), Al (Ref. 21), Mo (Ref. 22), Ta (Ref. 23), and austenetic (fcc) stainless steel[12], good agreement between theory and experiment is found.

From an interplay between theory and experiment, a simple picture has evolved which describes not only the interaction of hydrogen with defects in metals but also a vast number of other phenomena related to the metal-hydrogen system such as, e.g. the behaviour of interstitial hydrogen in solid solution, bulk and surface diffusion, the chemisorption of hydrogen at metal surfaces, and the molecular adsorption and dissociation process of hydrogen molecules at surfaces[7].

The basic idea behind the effective-medium theory[25] is to replace the complicated inhomogeneous metal host by a simpler host, the effective medium, for which the full quantum-mechanical calculation can be carried out in a proper self-consistent way. The corrections associated with the differences between the metal host and the effective medium are included perturbatively. For hydrogen interacting with a metal a convenient effective medium is the homogeneous electron gas of density $\bar{n}_0$, where $\bar{n}_0$ is a weighted average of the electron density around the hydrogen atoms in the metal. The embedding energy (total energy of combined systems minus that of the constituents) for a hydrogen atom at the position $\vec{R}$ in a transition metal host can be written as a sum over different terms[10,11]

$$\Delta E(R) = \Delta E^{\mathrm{eff}}_{\mathrm{hom}}(\bar{n}_0(\vec{R})) + \Delta E_c(\vec{R}) + \Delta E_v(\vec{R}) + \Delta E^{\mathrm{hyb}}(\vec{R}) . \qquad (1)$$

The dominating term $\Delta E^{\mathrm{eff}}_{\mathrm{hom}}(\bar{n}_0)$ represents the interaction between the hydrogen atom and a homogeneous electron gas and it depends only on $\bar{n}_0$. The three latter terms describe the corrections mentioned above: ΔE_v, the inhomogeneity of the real metal, ΔE_c, the interaction of hydrogen with the metal core electrons and, in the case of transition metals, the hybridization ΔE^{hyb} between the hydrogen state and the metal d band. The properties of the metal enter this expression through $\bar{n}_0$ and through the d-band and core-electron properties in the subsequent terms. The properties of the hydrogen atom however mainly enter through the term $\Delta E^{eff}_{hom}(\bar{n}_0)$. This function can be calculated once and for all as a function of the electron-gas density (see Fig. 1).

From the $\Delta E^{eff}_{hom}(\bar{n}_0)$ curve alone, it is possible to explain qualitatively the observed changes in potential energy when a free hydrogen atom outside the metal is moved through the surface into the bulk of the host (see Fig. 2). The electron density variations seen by the hydrogen atom as it passes into and through a metal along the path shown in Fig. 2a, is illustrated in Fig. 2b. Outside the surface, the electron density falls off exponentially to zero. Given the $\Delta E^{eff}_{hom}(\bar{n}_0)$ function for hydrogen, the potential energy variations can then be constructed as shown in Fig. 2c. As the hydrogen atom approaches the surface, it will encounter the optimum density at some point. This gives rise to the chemisorption minimum in which the atom binds outside the surface. Usually this is the most stable site of all because the density is higher than the optimum everywhere in a perfect lattice.

Moving further into the lattice, the density rises, and the $\Delta E^{eff}_{hom}(\bar{n}_0)$ function becomes almost linear in density. The energy variations are therefore a direct reflection of the variations in the metal-electron density. The sites of lowest energy will be the most open sites, octahedral (O_h)in fcc and tetrahedral

(T_h) in bcc. The activation energy reflects the minimum density change seen by the hydrogen atom moving from one site to the next. This energy is highest in the close-packed fcc and hcp structures, and diffusion is thus fastest in the bcc metals.

Any open defects will act as a trap for hydrogen since the energy is lowered due to the decrease in electron density. The more open the defect, the larger the trapping energy, which therefore increases in the sequence: dislocation $\lesssim$ vacancy $\lesssim$ void. At the center of a vacancy, the density is less than optimum, and therefore the hydrogen atom is displaced from the center site.

In the following, we shall limit our discussion to the trapping of D at defects in metals especially Pd.

Experimentally, we used ion implantation, nuclear reaction analysis and the channeling technique to determine the trap-binding enthalpies and the equilibrium positions of D at defects.

The experimental setup and method have been described in detail previously[8]. Very briefly, 10-15-keV D was *in situ* ion-implanted in single crystals of Pd at temperatures T~30-100 K. During subsequent linear-ramp annealing (1-2 K/min), the total amount and the depth distribution of the D within the first 0.5 μm was monitored with nuclear-reaction analysis, detecting either protons or α particles from the 750-keV ^{3}He-excited nuclear reaction D(^{3}He,α)p (Ref. 26). In some cases, the injection of D was preceded by room-temperature implantation of ^{4}He ions with a range approximately equal to that of D ions, ~1000-1500 Å. This created a dense array of ~10 Å diameter He bubbles as observed by TEM. The D-lattice location at selected temperatures was determined by ion channeling. To extract trap binding enthalpies, the retention- vs-temperature curves were modelled mathematically by a diffusion equation describing diffusion in a field of traps[13,9].

All the experimental details concerning the linear-ramp-annealing curves and the channeling data will be published in a subsequent paper[27]. Here we shall state only the results and discuss them in relation to the theory.

The strongest trap strength was observed when the Pd crystal prior to the low-temperature D implantation was preimplanted with $4x10^{16}$ He/cm^2, at room temperature. These bubbles were found to trap D with a binding enthalpy of 0.31 eV relative to the solution site.

To study the trapping of D to implantation defects such as vacancies, the Pd crystals were implanted with 10-keV D and fluences ranging from $3x10^{15}$ D/cm^2 to $4x10^{16}$ D/cm^2. The analysis of these studies were complicated by the fact that at the time D starts to depopulate from the vacancies, ≈200 K, the electropolished Pd surface constitutes a substantial barrier to D release. Therefore we used our previously developed two-trapping-layer technique[13,19] which allows us to distinguish unambiguously the matrix defect trapping from the surface-permeation barrier.

The detailed analysis of the linear-ramp annealing curves showed that the implantation damage trapped D with three different binding enthalpies, 0.31 eV, 0.23 eV, and 0.15 eV, respectively. The two first trap strength are ascribed to trapping at vacancy clusters and at monovacancies, respectively. By increasing the implantation fluence, a low-temperature annealing stage (0.15 eV) appeared and it is assigned to monovacancies with high deuterium occupancy.

For Pd and a number of other metals, the trap strength of D to monovacancies and He bubbles/voids are compared with the results of the effective medium-theory in Fig. 3. It is seen that all the trends are well described by the theory, and in addition there is also a good absolute agreement between theory and experiment. Palladium is special in the sense that the trap strengths for Pd are fairly low, a fact which is easy to explain within the theory. In vacancies, the electron density at the centre is below the optimum one for the ΔE_{hom}^{eff} curve in Fig. 1, and thus D will be trapped at a position displaced from the center of the vacancy corresponding to the optimum $\bar{n}_0$. The D-vacancy trap strength is then essentially the difference between the energy at the linear part of the curve corresponding to a solution site (the heat of solution) and the the minimum energy of Fig. 1. What makes Pd special in Fig. 3 is thus the fact that Pd has a low interstitial electron density, as compared to the other neighboring elements. Therefore the energy gained going from an interstitial site to the displaced vacancy site is less in Pd. This, by the way, also explain the unusually high solubility of hydrogen in Pd.

Since D is not trapped at the centre of the vacancy, there is room for more than one D in each vacancy, and for a vacancy in the fcc metal such as Pd, six D atoms can be trapped to a vacancy at positions displaced towards the octahedral positions next to the vacancy. The influence of the D-D interactions on the vacancy trap strength is incorporated by including the electron density from each D atom at the position of the others. In Fig. 4 the calculated[28] vacancy trapping energies

$$E(N) = E(N) - E(N-1) - E^{int} \qquad (2)$$

are shown together with the experimentally determined values as function of occupancy N for Pd, Nb, Cu, Mo, Ni, Fe. E^{int} is the interstitial binding energy at the solution site. It is seen that for the metals like Ni, Cu, Fe, and Mo, the binding energy for the first two D atoms are virtually the same, explained by the fact that they lie on opposite sites of the vacancy site opposing the O_h sites. For occupancies greater than two, the D-D interacts repulsively, causing a decrease in binding energy, in qualitative agreement with the experimental findings. The experiments were analyzed by assuming only two trap strengths. One for low (1-2) and one for high (3-6) occupancy of the vacancy.

Again Pd is special in the sense that multipel occupancy is most favorable in this metal. In fact, theoretically the D-D interactions are slightly attractive, again a result of the large lattice constant and thus the low interstitial electron density in Pd (Ref. 28).

The detailed lattice location of D trapped to vacancies in Pd are determined by the channeling technique[29]. After low fluence, low temperature implant, the D occupies the O_h interstitial site which is the solution site for D in the fcc metals, in agreement with the theory. To study the lattice location of D trapped at vacancies, the implanted Pd crystals were subjected to isochronal-annealing sequences for 15 min at temperatures ranging from 25 to ~200 K and then cooled to 25 K, where the measurements were performed. Around 80-100 K, D begins to populate the vacancy traps, and after annealing to 190 K, all the D are trapped by monovacancies with low occupancy. The experimental results (see Fig. 5) show that ≈35% of the D being displaced from the O_h site by ≈0.2 Å towards the vacancy, whereas the remaining ≈65% of the D atoms are displaced ≈0.2 Å from the T_h site towards the vacancy. The rms displacement amplitude of the D is fairly large, ≈0.25 Å, indicating that the D state is rather delocalised[18].

The experimental observations are again qualitatively explained by the effective-medium theory[18]. With the effective medium potential of the D in the vacancy, the Schrödinger equation has been solved. The resulting D ground-state density is clearly delocalized with maxima at sites displaced from the O_h site towards the vacancy and with rms displacement amplitudes of the same order as observed experimentally. However, the excited states for a D in the vacancy are clearly more tetrahedral-like, suggesting that excited vibrational states are populated already at the measuring temperature of 25 K. A similar population of excited vibrational states has been demonstrated in Ni[18].

In conclusion we have shown that based on the effective medium scheme a simple model has evolved which is able to give a qualitative and in many cases even quantitative understanding of observations concerning hydrogen interactions with metals. With respect to the trapping of hydrogen at defects we have shown that any dilution of the lattice leads to trap, and open defects like vacancies can trap up to six hydrogen atoms. However even in this case the distance between the six D atoms in a Pd vacancy (1.85 Å) are significantly larger than the interatomic distance in a D_2 molecule (0.74 Å). Thus it is difficult to see how defects can mediate an increase in the D-D tunneling probability and explain the proposed cold fusion.

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FIGURE CAPTIONS

Fig. 1. ΔE^{eff}_{hom} as a function of average electron density $\bar{n}_0$ in atomic units a_0^{-3}, a_0 being the Bohr radius.

Fig. 2. Schematic illustration of the construction of the energy variation of a hydrogen atom passing through a metal.

Fig. 3. Measured (open symbols) and calculated (filled symbols) trap-binding enthalpies (energies).

Fig. 4. Calculated trapping energy (Eq. (2) of deuterium as a function of D occupancy in monovacancies in Pd, Ni, Mo, Cu, Nb, and Fe. The solid lines are the experimental data (Ni, Ref. 19), (Fe, Ref. 14), (Cu, Ref. 20), (Mo, Ref. 22). The energies (in eV) are given relative to the trapping energy of the first D in the vacancy.

Fig. 5. Normalized channeling yields from D and Pd around the <100> axis after annealing at 190 K for 15 min. D was implanted at 25 K with an energy of 15 keV, to a fluence of 6×10^{14} D/cm^2. The dashed curve is the result of the multirow continuum-model calculation, assuming that 37% of D is displaced 0.2 Å from the O_h site towards the nearest-neighbor (vacancy) site, and 63% of D is displaced 0.15 Å from the T_h site towards the vacancy.

Fig. 1

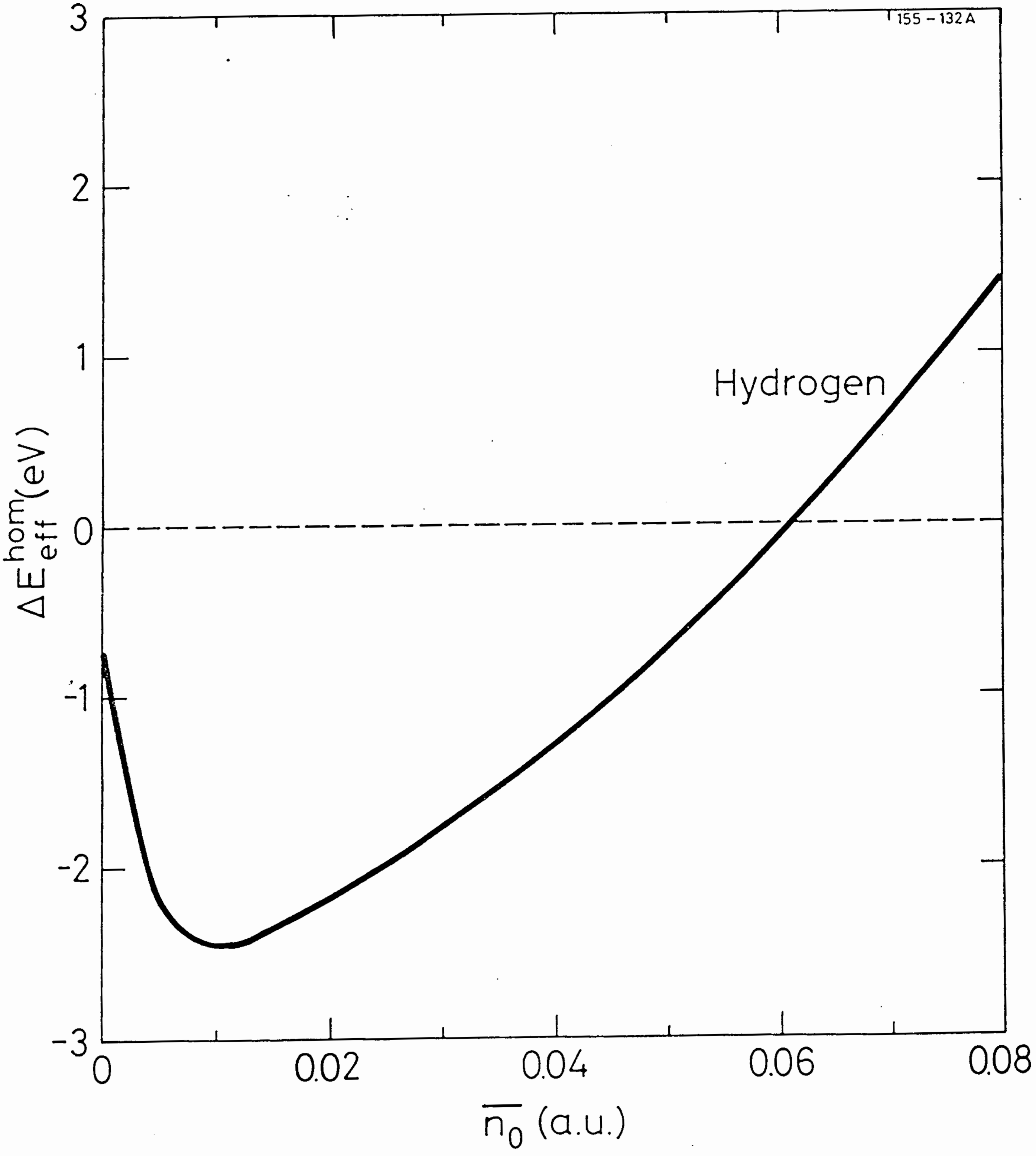

155 – 132 A
3
2
1
0
-1
-2
-3
ΔE_{eff}^{hom} (eV)
Hydrogen
0
0.02
0.04
0.06
0.08
$\overline{n_0}$ (a.u.)

Fig. 2

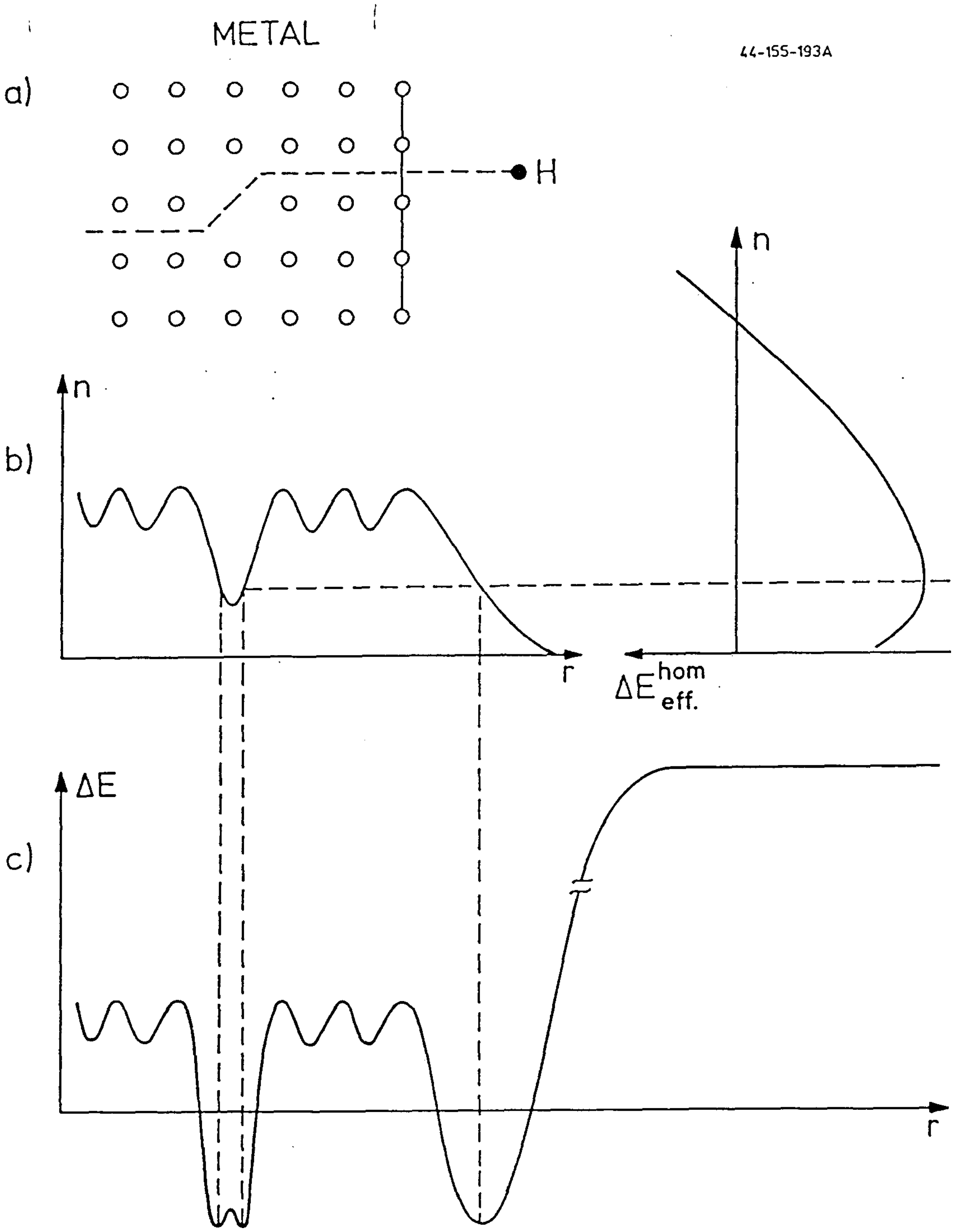


Fig. 3

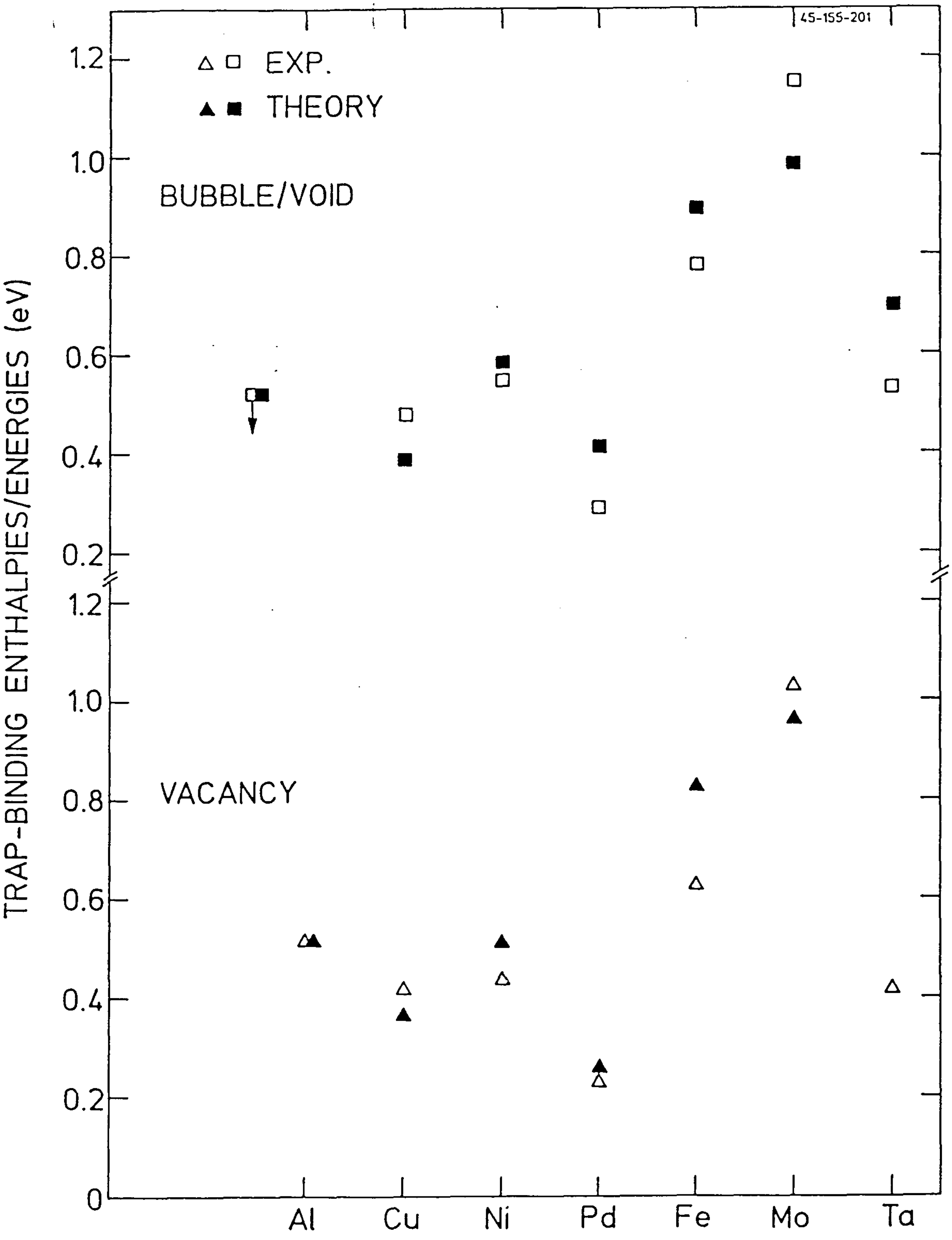

45-155-201
△ □ EXP.
▲ ■ THEORY
BUBBLE/VOID
VACANCY
TRAP-BINDING ENTHALPIES/ENERGIES (eV)
1.2
1.0
0.8
0.6
0.4
0.2
1.2
1.0
0.8
0.6
0.4
0.2
0
Al
Cu
Ni
Pd
Fe
Mo
Ta

Fig. 4

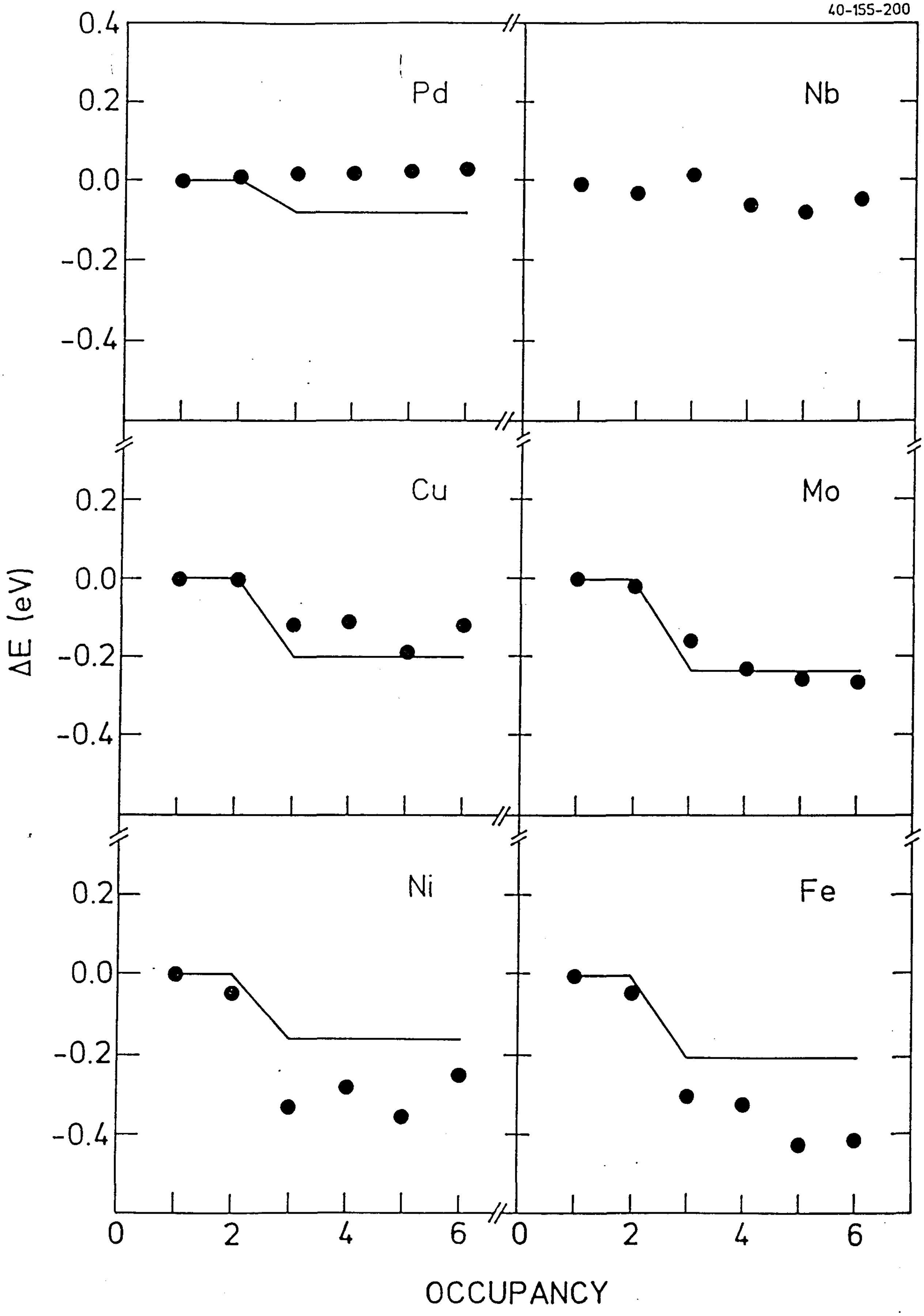
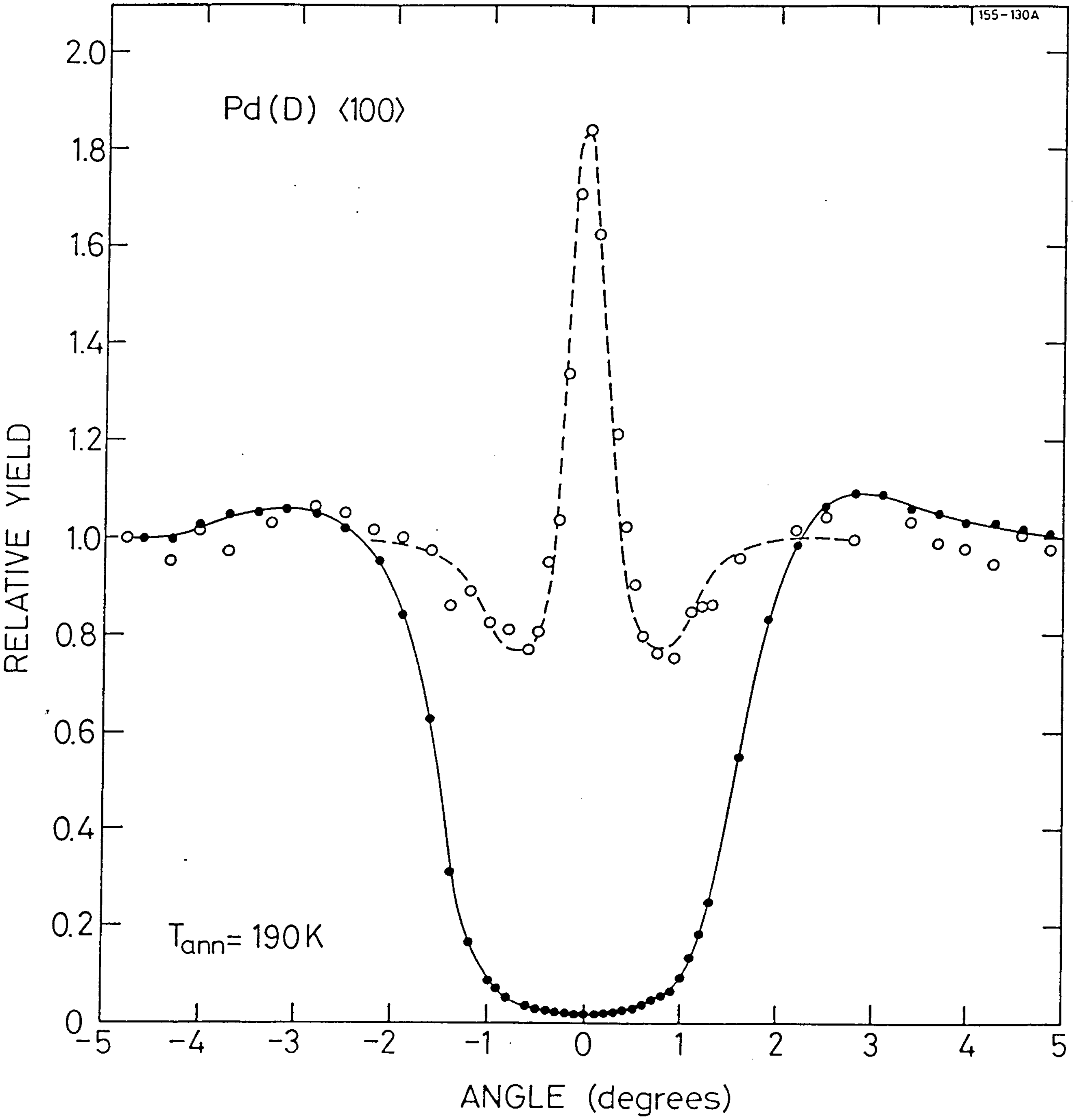


Fig. 5



155-130A
Pd(D) ⟨100⟩
T_{ann}= 190K
RELATIVE YIELD
ANGLE (degrees)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
−5
−4
−3
−2
−1
0
1
2
3
4
5