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Hydrogen and deuterium decoration of In-vacancy complexes in nickel

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The quantum-mechanical states of hydrogen and deuterium in pure and defected nickel have been calculated using the effective-medium theory. The defects considered include monovacancies, the substitutional In impurity, a complex of four vacancies, and a complex of an In impurity decorated with a tetrahedron of four vacancies. While the substitutional In impurity does not trap hydrogen, the vacancy and the vacancy complexes with and without In association do. The calculated binding energy to the four vacancy complex is nearly insensitive to the hydrogen isotopic mass and to the In decoration. These results, along with the dependence of the hydrogen binding energy on multiple hydrogen occupancy of the In vacancy complex, are compared with recent perturbed-angular-correlation experiments.

I. INTRODUCTION

The interaction of hydrogen with lattice defects in solids is a growing area of study in experimental and theoretical physics.¹ The perturbations created by defects due to lattice geometrical and electronic structure changes alter the location of the hydrogen site and its self-trapping energy. While experimental investigations of hydrogen trapping by *point* defects (e.g., monovacancies, substitutional and interstitial impurities) have been carried out for some time,^{2,3} the data on hydrogenation of metals containing *complex* defects (e.g., vacancy complexes) are just becoming available.^{4,5} These studies not only illustrate the electronic structure of defect complexes, but also how it is affected by hydrogen decoration.

In this paper we discuss a recent perturbed-angular-correlation experiment⁴ in In-doped Ni in the light of a theoretical study for this system. In their experiment Collins and Schuhmann measured the time evolution of the angular correlations between nuclear gamma rays, the decay cascade being perturbed by the hyperfine interaction between the nuclear moment and electric field at the ¹¹¹In probe nucleus in Ni under various sample conditions. Since these interactions are governed by local environments, the structure around the probe nucleus can be elucidated. The authors have studied substitutional In impurities (by diffusing In in pure Ni), In-vacancy complexes (by cold rolling the NiIn sample to introduce vacancies and by forming vacancy complexes through heat treatment) and In-hydrogen-vacancy complexes (by electrolytically charging the cold-rolled NiIn samples and then performing experiments as a function of temperature and hydrogen concentration). They have identified five different sites for In by measuring the hyperfine field and

the quadrupole frequency. These are: (i) a substitutional site (*S*), (ii) a cubic site (*C*) where In is relaxed into a tetrahedral site surrounded by four vacancies, (iii) a noncubic site (*M*) where In may be associated with extended defects such as dislocations or vacancy complexes which destroy cubic symmetry around In. When the samples are loaded with hydrogen, (iv) a new cubic site (*C_H*) and (v) a noncubic site (*M_H*) are separated. Site *C_H* is interpreted as a site *C* decorated by four hydrogen atoms bound in each of the four tetrahedrally oriented cavities around In. Sites *S* and *C* are easily identifiable since no quadrupolar interaction is possible at a probe nucleus with cubic symmetry. The structure of the site *C* is found to be especially stable and favored according to experiments⁶ and calculations.⁷ When the samples are loaded with hydrogen, the intensity of the site *S* is unchanged signifying that In at the substitutional site does not trap hydrogen. The intensities associated with sites *M* and *C* drop while sites *C_H* and *M_H* appear with site *C_H* gaining dominance over site *M_H* as hydrogen concentration is increased. Upon saturation, site *C* is completely suppressed. The authors also noted a damping of site *S* and *C* signals in hydrogen-loaded samples, which was attributed to fluctuating hyperfine interactions caused by hydrogen atoms diffusing near probe sites. This observation is particularly interesting since a single hydrogen atom delocalized in a tetrahedral configuration around In could also lead to the disappearance of quadrupole interaction. Thus, whether the cubic site *C_H* observed in hydrogen-loaded samples is due to a delocalized hydrogen (equivalent to a quantum mechanical picture) or four hydrogen atoms decorating the In along the tetrahedral bonds poses an interesting question.

In this paper we have carried out calculations to ad-

TABLE I. Self-trapping characteristics for hydrogen and deuterium at the octahedral site in *pure* Ni. The hydrogen energies E , E_α^∞ , and E_T are defined in Eqs. (1) and (2). The relaxation of the first (I) and second (II) nearest-neighbors are defined as the percentage change in the interstitial-site–host-atom distance.

| Isotope | E (eV) | E_α^∞ (eV) | E_T (eV) | Relaxation | |
|---------|----------|------------------------|------------|------------|----|
| | | | | I | II |
| H | −2.20 | −2.08 | 0.12 | 2.5% | 0% |
| D | −2.25 | −2.15 | 0.10 | 2.4% | 0% |

dress the above issues. We have calculated the energetics of hydrogen in pure Ni, Ni containing dilute substitutional In impurities, monovacancies and four-vacancy complexes, and In-vacancy complexes. Similar calculations are repeated for deuterium. We have also studied the effect of hydrogen concentration on trapping. Our theoretical method is outlined briefly in Sec. II. The results and their comparisons with experiment are described in Sec. III. A brief summary and the conclusions are given in Sec. IV.

II. THEORETICAL METHOD

Our calculations are based upon the effective-medium theory.^{8–10} The potential energy for a hydrogen atom at a given point is constructed by replacing the host with a homogeneous electron gas (effective medium) with a density equal to the average electron density seen by the embedded hydrogen atom. The major part of the hydrogen–host interaction is then described by the embedding energy of the impurity in the electron gas. Moreover, the covalent interaction of the hydrogen 1s state with the d electrons of the transition metal and the interaction with the metal core electrons are included.⁹ In practice, we calculate the host electron density by superimposing atomic-charge densities. Once the potential is obtained, we determine the quantum-mechanical state of the hydrogen by solving the three-dimensional Schrödinger equation for the hydrogen mass coordinates.¹¹

The calculations are first carried out for hydrogen in perfect Ni to determine the self-trapping energy.¹¹ The probability distribution of the self-trapped hydrogen and the potential gradient with respect to its mass coordinates are used to determine the Kanzaki forces. The forces in turn are used to calculate the displacements of the host atoms via the lattice Green’s function. The new positions of the host atoms determine a new charge density map and the corresponding hydrogen potential. The above process is repeated until self-consistency is achieved. The energy of the hydrogen coupled to the lattice can be written as

$$E = E_\alpha + E_L, \quad (1)$$

where E_α is the eigenvalue of the hydrogen Schrödinger equation and E_L is the elastic energy stored in the host atom displacements. The self-trapping energy is defined as

$$E_T = E_\alpha^\infty - E, \quad (2)$$

where E_α^∞ is the eigenvalue of the delocalized band state

with periodic boundary conditions and with no lattice distortion.

In the case of the lattice defects, which include here the monovacancy, the substitutional In, and the four-vacancy cluster with and without In, the lattice relaxation has been ignored before and after hydrogen decoration. The binding energy of hydrogen to a defect site is defined as the energy difference,

$$\Delta E = E^h - E^i, \quad (3)$$

where the superscripts h and i denote the perfect and imperfect host system, respectively. Defect trapping is possible if $\Delta E > 0$. Due to the omission of lattice distortion in the defect case, ΔE only accounts for “chemical” changes caused by the defects in the host matrix.

III. RESULTS

In Table I we present the various energies and displacements for the self-trapped states of hydrogen and deuterium in *pure* fcc Ni. The results are given for hydrogen at the octahedral interstitial site only since the self-trapping at the tetrahedral site is less favorable.¹¹

The binding energies of hydrogen associated with various trap configurations are given in Table II. Note that the substitutional In does not trap hydrogen. In this case, the trapped state is searched for by forcing the hydrogen wave function to be localized at an octahedral site adjacent to the In impurity. However, the electron density at this site increases over the ambient value. Such a situation has been demonstrated earlier not to lead to hydrogen trapping.^{12,13} The incorporation of lattice distortion caused by In could, however, alter the hydrogen trapping saturation.¹¹ The relative change in the lattice constant of

TABLE II. Binding energies ΔE [Eq. (3)] of hydrogen and deuterium to various defect environments in Ni.

| Isotope | Defect | ΔE (eV) |
|---------|----------------------------|-----------------|
| H | Substitutional In | −0.14 |
| D | Substitutional In | −0.14 |
| H | Monovacancy | 0.54 |
| D | Monovacancy | 0.45 |
| H | Four-vacancy complex | 0.47 |
| D | Four-vacancy complex | 0.44 |
| H | In four-vacancy complex | 0.45 |
| D | In four-vacancy complex | 0.42 |
| H | In four-vacancy 2H complex | 0.45 |
| D | In four-vacancy 2H complex | 0.41 |

Ni due to alloying with In is¹⁴

$$\Delta a / \Delta c = 5.3 \text{ \AA/at. \%} . \quad (4)$$

This outward displacement increases the volume available for hydrogen and the ensuing lattice strain would induce hydrogen trapping. However, the magnitude of this effect is typically few tens of meV and does not change the qualitative picture in Table II.¹³ Thus, substitutional In provides a very weak trap at best for hydrogen which explains the relative insensitivity of the *S*-site intensity upon hydrogenation.

On the contrary the monovacancy in Ni provides a strong trap site. In Fig. 1 we plot the potential and density distribution of hydrogen on the (110) plane. Note that hydrogen is off center from the vacancy and distributed mostly around the outer edge of the vacancy. This is because according to the effective medium theory the major tendency is that hydrogen seeks out to an optimum electron density of ~ 0.01 a.u. The delocalization and the ensuing zero-point energy depend on the isotope mass and therefore the binding energies for hydrogen and deuterium are slightly different. The present calculations reproduce the results of earlier similar calculations for deuterium trapped at a Ni vacancy.¹⁵ Moreover, the binding energy is in agreement with previous calculations² and experiments.^{2,4}

The potential and density distributions of hydrogen in a pure four-vacancy complex are plotted in Fig. 2. Unlike

in the case of the monovacancy, the hydrogen is fairly localized into the regions around the octahedral sites. The binding energies are relatively smaller than in the monovacancy and have a negligible isotope dependence. The slightly smaller binding energies compared to the monovacancy are due to the somewhat steeper potential wells in the case of the four-vacancy complex leading to a larger zero-point energy. The results for In four-vacancy complexes plotted in Fig. 3 are similar. The binding energies again show no isotope dependence and are not much different from the bare vacancy complexes. The former result is consistent with the tentative interpretation of Ref. 4. The latter issue is difficult to judge on the basis of the experiments.⁴ These suggest that the bare vacancy complexes might be slightly less attractive to hydrogen than those decorated with In, although this is not necessarily true due to experimental uncertainties. Also, our theoretical result is not fully conclusive, since our calculations do not take into account host-atom relaxations caused by the In four-vacancy complexes. However, our results show that there is no chemical affinity between the hydrogen and the In probe.

The nature of hydrogen density in Fig. 3 implies that if the In four-vacancy complexes were decorated with only one hydrogen, it would lead to a quadrupole interaction at the In nuclear site. This is because due to the relatively wide potential barrier the hydrogen wave function actually vanishes between the adjacent maxima leading to di-

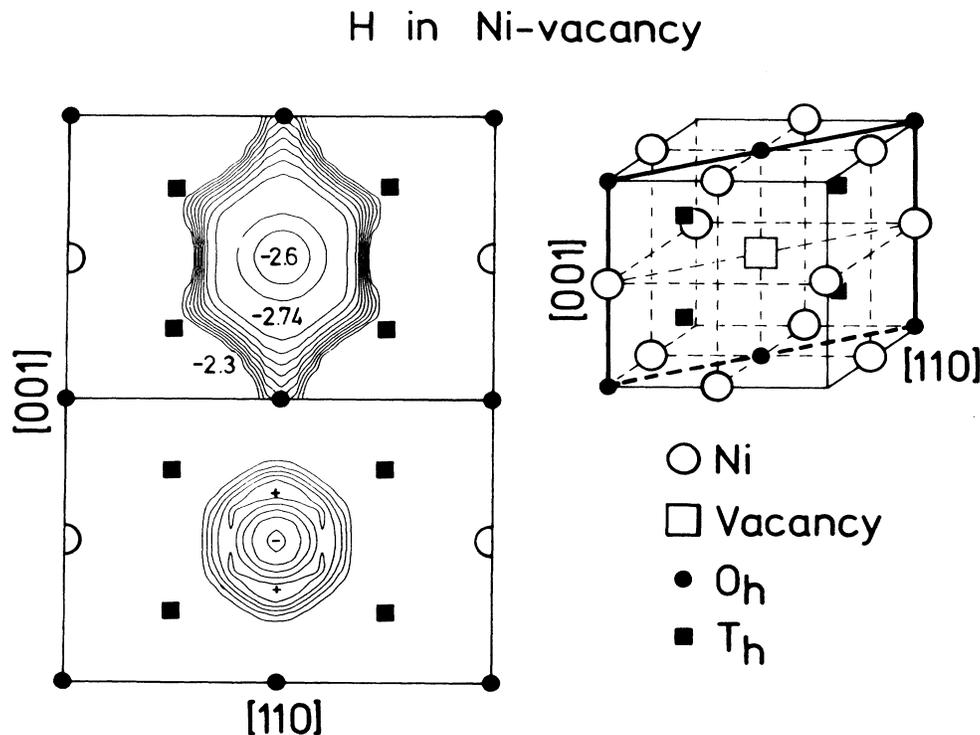


FIG. 1. Hydrogen trapped by a monovacancy in Ni. The upper contour plot gives the hydrogen potential (binding energy measured relative to free H_2 gas). Contour spacing is 0.05 eV. Contours above -2.3 eV are not shown. The lower contour plot gives the hydrogen density. Contour spacing is one sixth of the maximum density. The plots are drawn for the piece of the (110) plane shown to the right from the contour plots. Octahedral (O_h) and tetrahedral (T_h) sites are indicated by solid circles and squares, respectively.

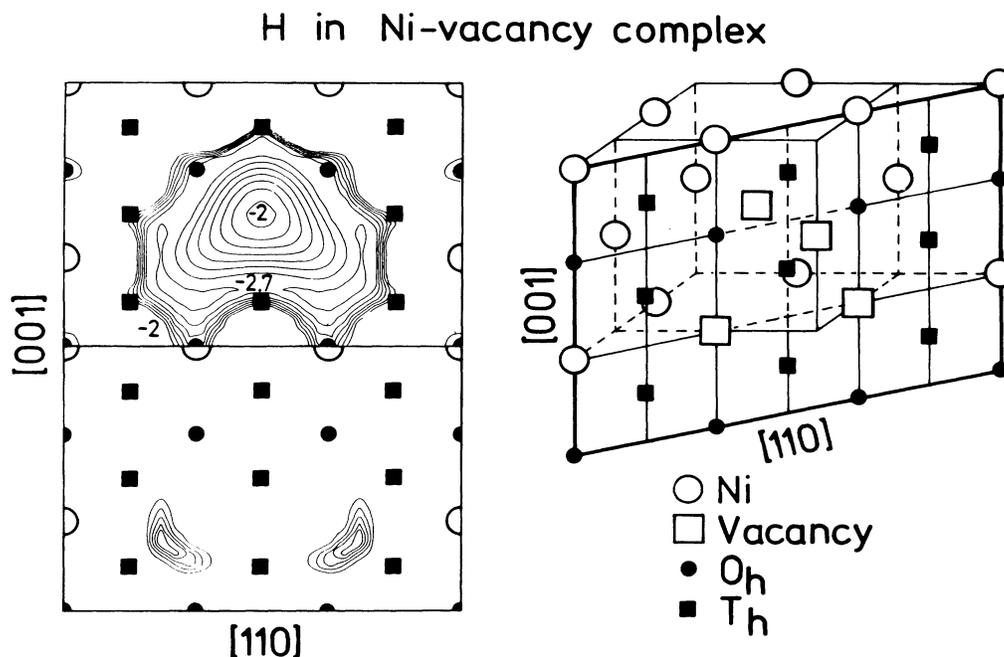


FIG. 2. Hydrogen trapped by a four-vacancy complex in Ni. The upper contour plot gives the hydrogen potential (binding energy measured relative to free H_2 gas). Contour spacing is 0.1 eV. Contours above -0.2 eV are not shown. The lower contour plot gives the hydrogen density. Contour spacing is one sixth of the maximum density. The plots are drawn for the piece of the (110) plane shown to the right from the contour plots. Octahedral (O_h) and tetrahedral (T_h) sites are indicated by solid circles and squares, respectively.

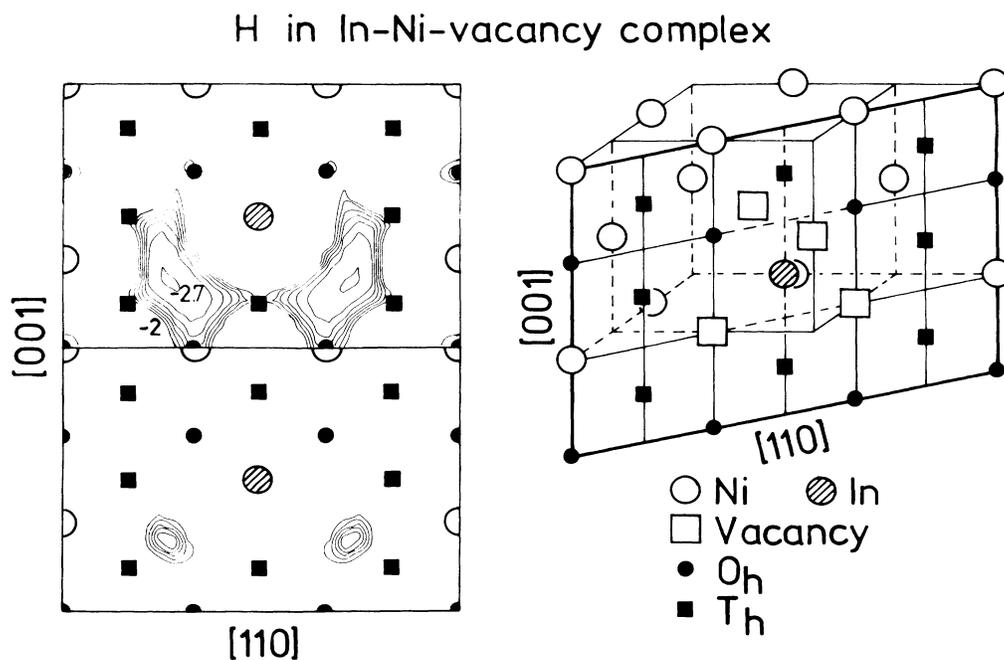


FIG. 3. Hydrogen trapped by an In four-vacancy complex in Ni. The upper contour plot gives the hydrogen potential (binding energy measured relative to free H_2 gas). Contour spacing is 0.1 eV. Contours above -2.0 eV are not shown. The lower contour plot gives the hydrogen density. Contour spacing is one sixth of the maximum density. The plots are drawn for the piece of the (110) plane to the right from the contour plots. Octahedral (O_h) and tetrahedral (T_h) sites are indicated by solid circles and squares.

minished tunneling and to the localization at one of the four corners of the complex. Thus the loss of the quadrupolar interaction has to be due to the decoration of the In-vacancy complexes by four hydrogen atoms situated in a tetrahedral coordination. To see if additional hydrogen trapping is possible, we began with an ambient system containing an In atom, four vacancies surrounding the In, and two H atoms statically located at two of the maxima of hydrogen density (Fig. 3). The charge densities for this system were evaluated in a manner described earlier. A third hydrogen atom was then introduced and treated quantum mechanically using the procedure already described. The binding energies for the third hydrogen and deuterium are given in Table II. Note that these energies are almost the same as those in In-vacancy complexes. Thus further decoration of the In-vacancy complexes by hydrogen is possible. Our results provide support for the assertion made by Collins and Schuhmann⁴ that In-vacancy complexes can be decorated with four hydrogen atoms.

IV. SUMMARY

The trapping characteristics of hydrogen to various defect sites in Ni have been studied using a comprehensive theory where the hydrogen potential is constructed using the effective-medium theory. The full quantum-

mechanical nature of hydrogen is taken into account by solving a three-dimensional Schrödinger equation. Our results confirm the interpretation provided in Ref. 4 for the perturbed-angular-correlation measurements on cold-rolled Ni, doped with ¹¹¹In. Our results can be summarized as follows. (i) Substitutional In impurity in Ni does not trap hydrogen. Thus, the signal intensity arising from the substitutional In would be unaffected upon hydrogenation. (ii) In-vacancy complexes in Ni provide an effective trap for hydrogen and can easily trap up to four hydrogen atoms. The binding energies of hydrogen are independent of isotope and are insensitive to either hydrogen or In decoration. Thus, upon hydrogen loading, all the defect sites (vacancy complexes, In-vacancy complexes, and In-vacancy complexes with partially filled hydrogen) are equally probable trap sites. The first kind of defect mentioned above cannot be seen in a perturbed-angular-correlation (PAC) experiment.

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