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Role of elastic and electronic interactions in trapping of hydrogen by impurities in transition metals

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The interplay between the lattice distortion and the electronic contributions to the trapping of migrating hydrogen isotopes by substitutional impurities is investigated. We use a comprehensive calculational scheme incorporating (i) the effective-medium theory for the electronic interaction, (ii) the lattice Green's function for elastic coupling, and (iii) the hydrogen quantum motion. The calculations for Ti and Cr impurities in V host show that lattice strain effects dominate. Cr, which otherwise provides an electronic trap site, does not induce trapping when elastic effects are incorporated. The situation in the case of Ti is just the reverse. We find no isotope dependence of the binding energy of hydrogen.

I. INTRODUCTION

A fundamental understanding of the phenomena related to trapping of hydrogen by lattice defects in metals still remains one of the most challenging problems in the study of metal-hydrogen systems.¹ For example, impurities (substitutional or interstitial) distort the geometric arrangement of host metal atoms in their vicinity. They also perturb the electronic structure of the host lattice. Introduction of hydrogen into this already defected system further perturbs the host electronic structure as well as leads to additional atomic displacements. In many instances, the hydrogen with its associated "cloud" of host-atom displacements (the *hydrogenic* polaron^{2,3}) may be trapped by the impurity, i.e., a finite amount of work is necessary to detach it from the impurity surroundings and move it to an impurity-free region.

It is difficult to say *a priori* whether the strain field produced by the impurity due to lattice atom mismatch is responsible for the trapping or whether it arises from the changes in the host electronic structure⁴ produced by the impurity. Moreover, a puzzling question is whether strain fields and electronic ("chemical") effects act in the same or opposite direction. The difficulty in answering these fundamental questions stems from the fact that one does not know accurately what kind of distortions impurities in, e.g., transition metals create in their vicinity. To complicate the problem further, the interaction of hydrogen with a metallic host cannot be treated quantitatively in linear-response theory or, for that matter, in terms of pairwise interatomic potentials. The light mass of hydro-

gen requires that it be treated as a quantum-mechanical particle. Notwithstanding these problems, many theoretical attempts have been made to explain the trapping of hydrogen.¹ It is only until recently that the trapping of hydrogen was considered to be governed primarily by elastic interactions.

In this paper we provide the first theoretical attempt where the effect of lattice distortion and perturbation of the electronic structure in the host produced by the impurity, the nonlinear interaction of hydrogen with metal electrons, the distortion produced by hydrogen in the defected host atomic structure, and the quantum-mechanical character of hydrogen are all taken into account. Our prescription is derived from first principles and is applied here to vanadium alloyed with Ti and Cr impurities. The reason for choosing these systems, in addition to the fact that recent experimental data^{5,6} are available, is that alloying V with Cr hardens the host metal whereas in alloying with Ti makes the system softer. This effect of the impurity atoms neighboring V in the Periodic Table allows one to systematically investigate the interplay of short-range electronic and long-range lattice distortion effect.

We find that the *electronic* structure effects in VCr induce hydrogen trapping while in VTi they *prohibit* trapping. On the contrary, the *elastic* effects produced by the changes in the lattice and elastic constants prohibit hydrogen trapping in VCr and induce trapping in VTi. We have repeated the calculations for deuterium, and the isotope dependence of trapping is discussed below.

It is clear that no theory can be designed to exactly account for all the problems associated with hydrogen trap-

ping discussed above. Therefore, approximations are inevitable. In the following we outline our theoretical procedure and carefully point out approximations wherever they are made.

II. THEORY

In recent publications^{3,4,7} we have described a comprehensive theory of hydrogen-metal systems, where one self-consistently (i) constructs the hydrogen potential-energy field using the effective-medium theory, (ii) includes the hydrogen quantum motion by explicitly solving the appropriate three-dimensional Schrödinger equation, and (iii) calculates the hydrogen-induced lattice distortions by using Green's-function techniques within the framework of lattice statics. The procedure is applicable to both extended (band) states and self-trapped or impurity-trapped states, and can also deal with isotope effects from the outset.

A crucial feature is the construction of the potential-energy surface $V(\mathbf{r})$ for hydrogen. This is accomplished⁸ by using the unperturbed host electron density $n(\mathbf{r})$ as the basic variable: the total interaction energy of the hydrogen with the metal at any given proton position is a functional of this density. This functional is nonlocal and density dependent, and does not reduce to a summation of pairwise interactions between the hydrogen and host atoms. It arises from the rather local electronic screening of the hydrogen by host *sp* conduction electrons and from the residual Coulomb, hybridization, and core orthogonalization contributions to the interaction. For more details and comparison with other approaches, the reader should consult Ref. 8. While the effective-medium functional is not known sufficiently accurately to predict interaction energies to a high quantitative precision, it can seemingly well reproduce the interesting qualitative features and systematics in, e.g., the transition-metal series.

Once the potential $V(\mathbf{r})$ is calculated for a given set of host-atom positions, the full three-dimensional Schrödinger equation is solved numerically by an iterative relaxation technique.³

The hydrogen probability distribution $|\psi(\mathbf{r})|^2$ is then used to determine the (Kanzaki) forces $\mathbf{F}(\mathbf{R}_i)$ exerted by the localized hydrogen on neighboring lattice atoms near positions \mathbf{R}_i . The forces in turn determine the displacements \mathbf{u} of the host atoms via the lattice Green's-function matrix \underline{G} . In shorthand notation,

$$\mathbf{u} = \underline{G}\mathbf{F}, \quad (1)$$

with

$$\mathbf{F}(\mathbf{R}_i) = - \int d\mathbf{r} |\psi(\mathbf{r})|^2 \frac{\partial V(\mathbf{R}_i + \mathbf{u}(\mathbf{R}_i) - \mathbf{r})}{\partial [\mathbf{R}_i + \mathbf{u}(\mathbf{R}_i) - \mathbf{r}]} \quad (2)$$

In Eq. (2) the derivative term is the force field due to the hydrogen-metal interaction.

The new (displaced) positions of the host atoms are then used to obtain a new electron density map and hydrogen potential, and the process is repeated until self-consistency is achieved. The electron density map is constructed by superimposing atomic densities, i.e.,

$$n(\mathbf{r}) = \sum_{\mathbf{R}_i} n_{\text{at}}(\mathbf{r} - \mathbf{R}_i). \quad (3)$$

In principle, the electron density determined self-consistently for each case, either with or without impurities, should be used. Such data are not readily available for transition-metal systems of interest here. The errors in the electron density in the important regions are, however, fairly small (≈ 10 – 20%) and the concomitant errors in the potential-energy surface do not change the *qualitative* results.

The static Green's function \underline{G} (inverse of the dynamic matrix) is a property of the host alone, and can in the harmonic approximation, be obtained from discrete lattice phonon data.⁹ Alternatively, one can use the elastic continuum model, which contains the Voight elastic constants and the Debye cutoff as parameters. For clean metals, discrete lattice Green's functions can be obtained, whereas for alloy systems detailed phonon data is lacking. For the latter, one has to calculate \underline{G} from the elastic continuum model. In what follows, we use for the impurity-containing host a lattice Green's function obtained from elastic theory, incorporating for each system the (local) changes in the elastic constants as observed experimentally for vanadium-based dilute alloys.^{10,11} The change in the Debye cutoff follows from the observed change in the equilibrium lattice constant.¹²

The energy of the trapped hydrogen coupled to the lattice can be written as

$$E = E_\alpha + E_L, \quad (4)$$

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 trapping energy gain is defined as

$$E_T = E_\alpha^\infty - E, \quad (5)$$

where E_α^∞ is the eigenvalue for a delocalized band state with periodic boundary conditions and no lattice distortions. The binding energy to host impurity is

$$\Delta E = E^h - E^i, \quad (6)$$

where the superscripts *h* and *i* denote the perfect and the impurity-containing host system, respectively. Impurity trapping occurs if $\Delta E > 0$.

III. TRAPPING BY A SINGLE IMPURITY

Table I first summarizes our results for the self-trapping of H and D in *pure* V. As in Nb, the tetrahedral (*T*) site has the lowest energy. The hydrogen-induced relaxations for the two nearest host-atom shells are also given. In the case of H, we have used both the discrete lattice and elastic continuum Green's functions, and Table I shows the differences between the two cases to be small. This justifies the use of the elastic model in what follows.

Also given in Table I are the purely *electronic* contributions to the hydrogen-impurity interactions obtained by freezing the host atoms in their perfect lattice positions and by replacing one of the atoms by an impurity (Ti or Cr). Thus the elastic energy E_L does not change, but E_α

TABLE I. Self-trapping characteristics for hydrogen isotopes in the tetrahedral (T) site of pure bcc V. E denotes the elastic and L the discrete lattice Green's function. E_α is the energy eigenvalue, E_L the elastic energy stored in the lattice, and E_α^∞ the energy eigenvalue for a delocalized state. E_T is the self-trapping energy. The average relaxations are given for the two nearest-neighbor shells (positive sign indicates outward relaxation). The last two columns give the purely *electronic* trapping energies when one of the neighboring atoms around the T site is replaced by an impurity (Ti or Cr); a positive sign indicates binding.

Isotope	Green's function	E_α (eV)	E_L (eV)	E_α^∞ (eV)	E_T (eV)	Relaxations		ΔE_{el} (meV)	
						I	II	Ti	Cr
H	E	-1.914	0.166	-1.498	0.25	7.5%	-0.2%	-3	7
H	L	-1.815	0.149	-1.498	0.17	5.1%	-0.4%	-3	7
D	E	-1.947	0.156	-1.611	0.18	7.2%	-0.1%	-3	7

changes due to a different potential energy $V(r)$. By the nature of the effective-medium functional, the "chemical" changes are in the present case such that due to the more compact electron cloud a substitutional element to the right in the Periodic Table (Cr) will bind H and D, whereas the one to the left (Ti) will not. The results for H are again independent of which Green's function is used. The purely electronic binding energy for the Cr impurity in V is very small (~ 7 meV) and independent of the isotope. Our results are opposite to those predicted by Shirley and Hall,¹³ who used a semiempirical model based on the difference in the valence electron number between the impurity and the host.

Next, we turn to a discussion of the combined effect of lattice strain and electronic changes on impurity trapping. This is accomplished by considering dilute alloys $V_{1-x}Cr_x$ and $V_{1-x}Ti_x$. We assume that the immediate surroundings of a single impurity has properties of an alloy with a finite concentration of impurity atoms. A single impurity and its nearest neighbors can be simulated by an alloy with an impurity concentration x of the order of 10 at.%. We obtain the positions of the relaxed near-neighbor V atoms around the impurity from the known change of the lattice constant upon alloying.¹² For Cr, this relaxation is inwards and amounts to

$$\frac{\Delta a}{\Delta c} = -1.9 \times 10^{-3} \text{ \AA/at. \%}$$

for small concentrations. On the other hand, in VTi the local distance increases since

$$\frac{\Delta a}{\Delta c} = 2.3 \times 10^{-3} \text{ \AA/at. \%}$$

Secondly, we use the *alloy* Green's functions for the elastic response. The changes in the elastic constants are ob-

tained from ultrasonic measurements.^{10,11} For example, the difference $c_{11} - c_{12}$ increases (decreases) linearly with concentration of Cr (Ti) impurities, whereas c_{44} remains practically unchanged. The Debye cutoff is changed according to the lattice constant change of the alloy. These changes reflect the fact that added Cr (Ti) hardens (softens) the vanadium metal, which is also seen in measured values of the bulk moduli. The atomic displacements due to hydrogen are calculated using the alloy Green's functions, where after one of the neighboring atoms is substituted by the impurity for the final-energy calculation.

The results are collected in Table II. If we assume that the elastic response to hydrogen near the impurity is similar to that in an alloy with 10-at. % concentration, we observe for Cr that the impurity-induced lattice strain acts to destabilize the electronic binding discussed above. The net effect is that Cr impurities in V do *not* trap either H or D.

For Ti impurities in V, the situation is opposite. While electronic effects alone lead to repulsion of H by the impurity, we predict that the lattice strain contribution more than compensates this and leads to hydrogen trapping. Already, the changes in lattice and elastic constants corresponding to $V_{0.95}Ti_{0.5}$ alloy would give a trapping energy of 23 meV. The two isotopes of hydrogen behave very similarly, and we predict a very small isotope effect for the trapping energy.

The alloy model for the impurity gives the qualitative prediction that Ti acts as a trapping site for hydrogen, but Cr does not, and that the balance is dominated by the elastic effects which, in this case, are opposite to the electronic contribution. For more quantitative calculations detailed information about the response of the V atoms to the substitutional impurity is necessary. Shirley and Hall¹³ have calculated the strain interaction between the

TABLE II. Impurity trapping of hydrogen isotopes in V. E_α is the energy eigenvalue, E_L the elastic energy, and ΔE the overall trapping energy. $\Delta E > 0$ indicates binding. Alloy data corresponding to a 10-at. % concentration are used for the lattice response. The average relaxations are given for the two nearest-neighbor shells (positive sign indicates outward relaxation).

Isotope	Impurity	E_α (eV)	E_L (eV)	Relaxations		ΔE (meV)
				I	II	
H	Cr	-1.915	0.174	7.9%	-0.1%	-6
H	Ti	-1.940	0.148	6.6%	-0.2%	45
D	Cr	-1.955	0.164	7.7%	-0.1%	0
D	Ti	-1.971	0.137	6.5%	-0.1%	42

impurity and hydrogen using the continuum theory of elasticity. Their results agree qualitatively with ours.

IV. COMPARISON WITH EXPERIMENTS

Pine and Cotts⁵ have recently measured the diffusion constant of H and D in VTi and VCr alloys. They find that activation energies for diffusion are larger in the alloy than in pure vanadium. A kinetic two-state trapping model involving both normal and impurity-bound interstitial sites for hopping hydrogen could not, however, consistently explain the data. Pine and Cotts tentatively conclude that Ti impurities trap hydrogen, with the binding energy increasing with Ti concentration. For a Ti concentration of 3 at.%, they find the trapping energy of 30 meV, which is in good agreement with our estimate for the low-concentration limit. However, their fit to the two-state trapping model gives a large isotope effect in contrast to our results.

For VCr alloys, the application of the two-state trapping model gives a binding energy of the order of 50 meV,¹⁴ but the overall fit to the data is not as good as in the case of VTi. Our model does *not* predict trapping of hydrogen to Cr in V. However, the alloying effects are such that an *increase* in the activation energy for diffusion is predicted, in agreement with the experimental data. Unfortunately, the effective-medium theory cannot predict quantitatively accurate activation energies, but gives a result³ that going from pure V to pure Cr increases the activation energy by a factor of 3. This suggests a 30% increase in the activation energy for a 10-at.% alloy, in qualitative agreement with experiment. In the small-polaron model,^{2,3} the diffusion mechanism in bcc metals is the one where the hydrogen continuously deforms the lattice in its path along $T \rightarrow O \rightarrow T$ chains. The activation energy is proportional to the $T-O$ energy difference.

The small-polaron model also explains the observed isotope effect in pure V, where D has the higher activation energy. It is interesting to note that Pine and Cotts observe the activation energy for D to fall below that of H in the alloys containing more than 10 at.% of Cr. This can be explained by the larger zero-point amplitude of H: As the Cr content is increased, H will feel the hardening effect sooner and its activation energy ($T-O$ energy difference) will increase more rapidly than that of D.

The interplay between the effects of elastic distortion and electronic structure on the trapping of hydrogen by substitutional impurities can also be used to shed new light on the interpretation of hydrogen energetics in NbCr and NbTi alloys. Recently, Richter *et al.*¹⁵ have observed, using inelastic neutron scattering, that the binding energy of hydrogen to Ti is larger than that to a Cr impurity in Nb host. The average change¹² in the lattice

constant, $\Delta a / \Delta c$ in NbTi is $-0.32 \times 10^{-3} \text{ \AA/at. \%}$ and in NbCr is $-5.69 \times 10^{-3} \text{ \AA/at. \%}$. These data suggest that the elastic distortion due to Cr is larger than that due to Ti. According to the present calculation, we could conclude that hydrogen cannot be trapped to either Ti or Cr in Nb host purely due to elastic distortion effects, since in both cases the host lattice is found to harden upon alloying. In a recent publication,⁴ we examined the effect of electronic structure on hydrogen trapping in Nb alloys. We calculated the binding energy of hydrogen to Cr and Ti to be 130 and 100 meV, respectively. This trend, however, is in contradiction to experimental results where the binding energy to Cr was found to be less than that to Ti. Since lattice hardening is found to prevent trapping, we believe that the elastic distortion effects in NbCr would reduce the hydrogen binding energy more than in NbTi, thus bringing the theoretical result in line with experiment. It is difficult to calculate the trapping energies in Nb alloys using both elastic and electronic effects (as done in the present work) since the lattice Green's function based upon the elastic continuum theory is not a good approximation for Nb-based alloys.³

V. CONCLUSION

Both lattice strain and short-range electronic effects play a role in hydrogen trapping by impurities. In the case of Ti and Cr impurities, the electronic contributions are small and trapping is dominated by the strain effects. In the low-density limit, Ti impurities trap H with a binding energy of the order of 40 meV. This is due to local lattice expansion and softening. The situation is reversed for Cr, where the lattice response renders electronic trapping inoperable. A finite concentration of Cr increases the activation energy for diffusion of H by decreasing the lattice constant and by hardening the lattice. Thus, both Ti and Cr alloyed into V lead to a lowering of the diffusivity of interstitial H, but for different reasons: Ti traps hydrogen, whereas Cr increases the diffusion barrier.

The computational method employed here is quite general, and can be applied for gaining a better understanding of several subtle phenomena related to hydrogen and muon¹⁶ trapping by impurities.

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