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Hydrogen and deuterium decoration of a vacancy complex in Ni

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Using perturbed angular correlations, we observed decoration of a well-known ^{111}In-vacancy complex in Ni with diffusing H or D atoms. Both partially decorated and saturated configurations are distinguished from the undecorated complex. The saturated configuration is believed to have one hydrogen atom bound in each cavity of vacancy size. Analysis of hydrogen detrapping above 300 K leads to a binding enthalpy ~0.6 eV, independent of isotopic mass.

INTRODUCTION

Interaction of hydrogen (H) with defects in metals has direct relevance to hydrogen transport and embrittlement. Recent studies of deuterium release using ion-beam profiling methods have indicated that lattice vacancies are significant trapping centers for hydrogen, with binding enthalpies ~0.5 eV in many metals.[1,2] In the present work we apply perturbed angular correlations of γ rays (PAC) to study trapping of H at a specific In-vacancy complex in Ni. The measurements are sensitive to the number of trapped H atoms, with distinctive signals observed when the complex is partially decorated or saturated with H atoms.

EXPERIMENT AND RESULTS

The angular correlation between γ rays in a nuclear cascade is perturbed by hyperfine interactions between the nuclear moments and electronic fields which arise in the local environment. The perturbations can provide unique signals which "flag" different lattice locations. As shown in recent reviews,[3,4] PAC studies on metals have been used to distinguish substitutional lattice sites and defect-associated sites created by trapping of intrinsic lattice defects at impurity probe atoms. Here we use the 171-245-keV cascade of ^{111}Cd following decay of 2.8-d ^{111}In. In past studies on Ni,[5,6] three relevant sites have been identified via the hyperfine field H_{hf} and the nuclear quadrupole coupling frequency ω_0. These sites, S, M, and C, are described in Table I together with H-associated sites observed for the first time in this study. For present purposes, the most important is C, with a reduced hyperfine field and zero quadrupole interaction characteristic of cubic site symmetry. Site C is believed to arise via relaxation of the probe atom from a substitutional lattice site to the center of a tetrahedron of vacant lattice sites.[5] The structure, shown in Fig. 1, is further supported by molecular statics calculations[7] and by channeling measurements.[8]

Samples were doped with undecorated C complexes as in previous work:[9] (1) carrier-free ^{111}In activity was diffused into 25-μm thick, 99.998% pure Ni foils; (2) foils were deformed by rolling at 295 K to introduce vacancies; and (3) rolled foils were annealed at 500 K for 15 min to

TABLE I. Lattice sites and hyperfine interactions. Measurements at 295 K. Tabulated data are from this study, except for site M. H_{hf} was derived from ω_L using $g = -0.306(1)$ [H. Bertschat *et al.*, Z. Phys. **270**, 203 (1974)].

Label	H_{hf} (kG)	ω_0 (Mrad/s)	Site description
S	$-66.8(1)$	~0	substitutional, defect-free In[a]
C	$-26.9(1)$	~0	cubic, relaxed 3-V complex[a]
M	26(3)	67(8)	extended defect cluster[b]
M_{H}	$7-19$	$10-20$	partially decorated site[c,d]
C_{H}	$+1.1(3)$	~0	cubic, fully decorated site[c]

[a] Reference 5.

[b] Reference 7. Site M is the same as site MQ_3 in Ref. 6, and probably the same at site B_1 of Ref. 5, from which H_{hf} is quoted.

[c] This work.

[d] The signal is fitted as a frequency $\omega = 44$ Mrad/s with strong damping. Comparison to Fig. 1(a) of Ref. 11 leads to two interpretations, depending on whether ω_L or ω_0 is dominant; model A: $\omega_L = \omega/2 = 22$ Mrad/s and $\omega_L > \omega_0 > \omega_L/2$; model B: $\omega_0 = \omega/3 = 15$ Mrad/s and $\omega_0 > \omega_L > \omega_0/3$. Tabulated ranges span both models.

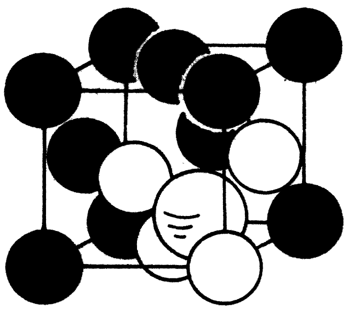

FIG. 1. Site C, consisting of an oversized impurity atom relaxed to the center of a tetrahedron of vacant lattice sites.

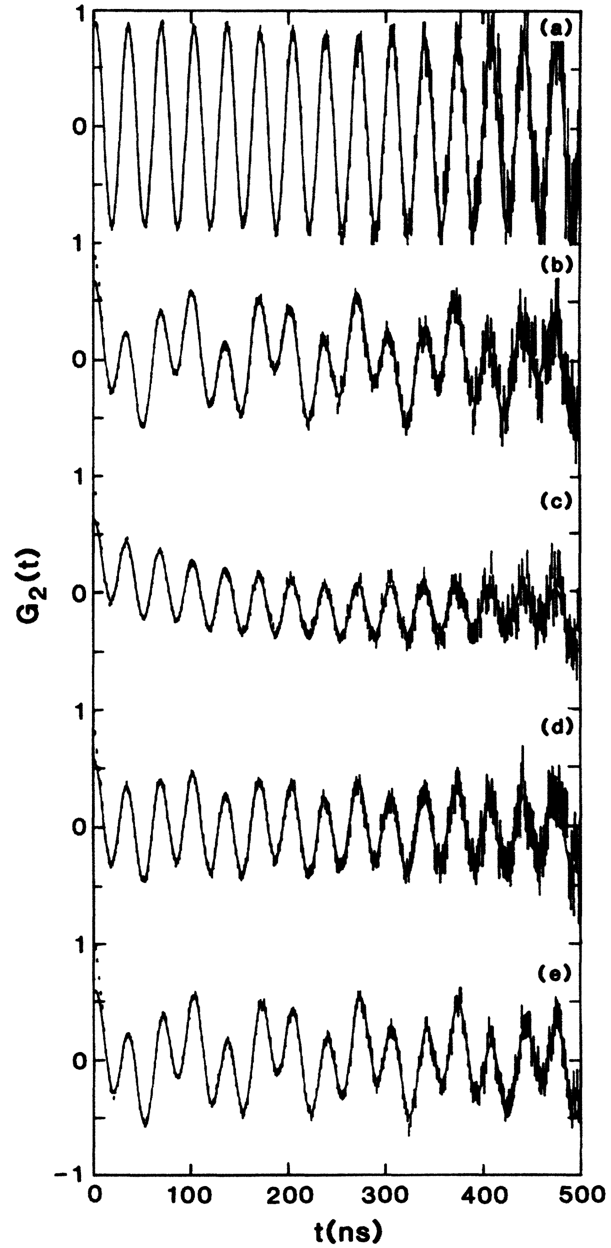

FIG. 2. ^{111}In PAC perturbation spectra for a Ni sample which (a) has been diffused with probe atoms, (b) doped with C sites, (c) loaded with H, (d) annealed at 323 K, and (e) 373 K.

form the C complexes. The 500-K annealing results in complete recovery of lattice vacancies, except those bound tightly in complexes.[6] The samples were then electrolytically charged with hydrogen (H or D) at 20 mA cm^{-2} in a 0.005M sulfuric acid bath containing traces of $NaAsO_2$. Hydrogen diffuses rapidly through the foils during charging at room temperature. Most PAC measurements were made using a spectrometer with four counters set at 90° angles and a transverse polarizing field of 3.5 kG.[10]

Typical spectra showing PAC perturbation functions[10] $G_2(t)$ are displayed in Fig. 2. Following diffusion of In, most probes are at substitutional sites S, with a pure magnetic Larmor frequency $2\omega_L = 185$ Mrad/s corresponding to a hyperfine field of 66.8 kG [Fig. 2(a)]. After doping with C sites, the fraction of S is reduced from near unity to ~30% while the C fraction, with $2\omega_L = 75$ Mrad/s, increases to ~30% [Fig. 2(b)]. The remaining atoms are at sites M, with mixed magnetic and quadrupole interactions producing an indistinct, attenuated signal.[11] In deformed metals, sites M are attributed to probes at the side of extended defect clusters.[6] After prolonged hydrogen charging, the S fraction is unchanged while C is entirely suppressed [Fig. 2(c)], indicating weak binding of H at substitutional sites S and strong binding in the C complexes. Computer analysis of spectra for hydrogen-loaded samples helped identify two hydrogen-decorated sites: M_{H} and C_{H} (Table I). Like site M, site M_{H} has an indistinct signal not clearly visible in the figure. Site C_{H} is evident in Fig. 2(c) as a low frequency precession. Analysis of other spectra taken with counter pairs at ± 135° (cf. Ref. 10) prove that C_{H} has a pure magnetic interaction, with a very small hyperfine field directed *opposite* to the fields at S and C. Absence of detectable quadrupole interactions for site C_{H} indicates cubic charge symmetry about the probe. Finally, annealing for 15 min at 323 K leads to loss of site C_H and partial reappearance of site C [Fig. 2(d)], while all evidence of H trapping is eliminated after annealing at 373 K [Fig. 2(e)]. Elsewhere, we will describe other features of the spectra, including damping of site signals attributed to fluctuating hyperfine interactions caused by H atoms diffusing near the probes.[12]

Saturation behavior. The effect of H dose was studied for charging times ranging up to 1 h , as shown in Fig. 3.

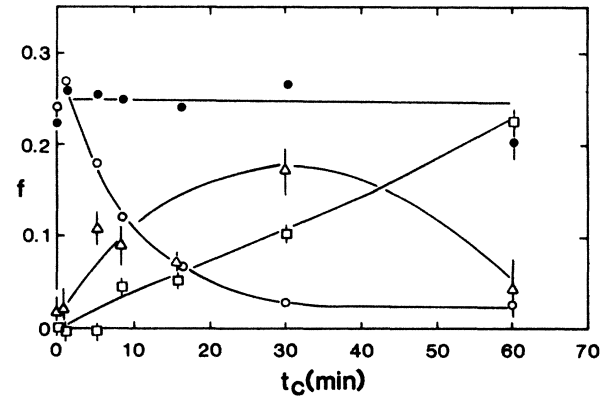

FIG. 3. Variation of site fractions with charging time t_c: site S (●), site C (○), site M_{H} (△), and site C_{H} (□).

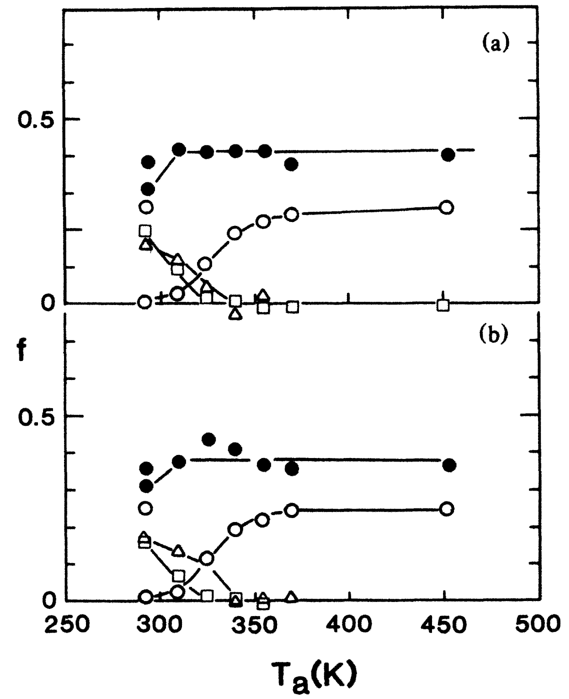

FIG. 4. Site fractions measured following 15-min isochronal annealings of (a) H-charged and (b) D-charged samples. For symbols, see Fig. 3 caption. The fractions of sites S and C prior to and following charging are both indicated at 295 K.

As charging proceeds, the fraction of site C (undecorated complexes) decreases while sites M_{H} and C_{H} increase. After prolonged charging M_{H} decreases while C_{H} saturates at the initial level of site C.[13] These observations suggest that M_{H} is created first and C_{H} forms by additional trapping.[14]

Annealing behavior. Site fractions were monitored during 15 min isochronal annealing of H and D loaded samples. We used a single C-doped foil cut in two pieces and took great care to give both samples identical treatments. As shown in Fig. 4, in both cases site C recovers to its original fraction during warming over the range 300–370 K while M_{H} and C_{H} disappear. Remarkably, close examination of the data shown in Fig. 4 indicates near exact coincidence (within ~1 K) between the reappearances of site C for the H and D charged samples.

DISCUSSION

Nature of the H-decorated sites. The dose dependences in Fig. 3 are explained naturally by the hypothesis that sites M_{H} and C_{H} are, respectively, partially and fully decorated counterparts of site C. The simplest configuration with cubic symmetry for site C_{H} has equal numbers of H atoms trapped in each of four vacancy "pockets" surrounding the probe atom (cf. Fig. 1). In this regard, recent effective-medium calculations of the binding of multiple H atoms in isolated vacancies in Ni are of interest.[15] Results indicate that the first two guest atoms can be accommodated on opposite sides of the vacancy center, each bound by ~0.5 eV, while additional H atoms induce significant H-H repulsion and are bound by only ~0.25 eV.[15] For complex C, the geometry of each of the four vacant sites surrounding the probe is restricted by the tetrahedral interstitial probe atom (see Fig. 1), so that placement of two H atoms on opposite sides of a vacancy center is not possible. We therefore conclude that the saturated C_{H} configuration involves only one H atom trapped in each vacancy pocket. For site M_{H}, lack of cubic symmetry, the transitory behavior observed in Fig. 3, and rough equality between the sum of the C_{H} and M_{H} fractions and the C fraction in Figs. 3 and 4 are all explained by the hypothesis that it involves the C complex decorated by 1, 2, or 3 hydrogen atoms.

Binding enthalpy. We analyze the reappearance of site C in Fig. 4 using a single-step detrapping model applied in previous work.[16] The detrapping rate is given by

$$\Gamma = g\nu\exp[-(E^M+E^B)/k_BT] \ , \qquad (1)$$

in which $g=12$ is a geometrical factor, $\nu=1.7\times10^{13}\ \mathrm{s}^{-1}$ is a jump-attempt frequency, and E^M and E^B are migration and binding enthalpies of the trapped atom. For the deuterium-loaded sample, Fig. 4(b), best computer simulations were achieved with $(E_{\mathrm{D}}^M+E_{\mathrm{D}}^B)=1.14$ eV, and using the value[17,18] $E_{\mathrm{D}}^M=0.41$ eV, we obtain $E_{\mathrm{D}}^B=0.74$ eV. This result is about 0.25 eV larger than found in H release measurements made via ion-beam profiling,[2,15] a difference too large to be explained by the simplicity of the detrapping model used here (see *note added in proof*).

What is the origin of the discrepancy? While our measurements are made on isolated trapping centers, the release studies involve vacancy concentrations up to 1%.[15] Under the latter conditions effective migration and binding enthalpies might be reduced, so that the two kinds of measurements are not comparable. On the other hand, our value 0.74 eV exceeds an upper bound of 0.6 eV suggested for binding of H to vacancies or voids in Ni.[19] The unusual strength of binding we observe might indicate chemical affinity between hydrogen and the In impurity, just as in release studies[20] (see *note added in proof*).

Effect of isotropic mass. Analysis of the reappearance curves for site C in Fig. 4 permits a precise determination of the difference of binding enthalpies $E_{\mathrm{H}}^B-E_{\mathrm{D}}^B$, as follows. According to classical rate theory, only the jump-attempt frequency depends on isotopic mass, $\nu \sim m^{-1/2}$. Since the curves overlap precisely, we set the detrapping rates for H and D equal, from which, for $T\sim330$ K, one obtains $(E_{\mathrm{H}}^M-E_{\mathrm{D}}^M)+(E_{\mathrm{H}}^B-E_{\mathrm{D}}^B)=k_BT\ln(2^{1/2})=+0.010$ eV. Using measured differences for $(E_{\mathrm{H}}^M-E_{\mathrm{D}}^M)$ equal to 0.012 eV (Ref. 17) and 0.008 eV,[18] we obtain as a final result $(E_{\mathrm{H}}^B-E_{\mathrm{D}}^B)=0\pm0.002$ eV. The fact that E^B depends less on isotopic mass than E^M, suggests smaller effects of quantum behavior on binding than on diffusion.

Summary. The present work demonstrates a new, microscopic approach to the study of H-vacancy interactions in metals. PAC experiments using other hosts and vacancy complexes are planned to determine systematic trends in hydrogen binding.

Note added in proof. The detrapping model applied above does not account for retrapping of lattice hydrogen at vacant trap sites. Diffusion of hydrogen in the presence of traps leads to a modified diffusion coefficient.[21] In our situation, it can be shown that the following approximate relation applies:

$$E^B = k_B T \ln(4tD_0/Al^2) - E^M \ , \qquad (2)$$

in which $T \sim 330$ K is the release temperature, $t \sim 900$ s is the annealing time, $D_0 \sim 5 \times 10^{-3}$ cm^{2}s^{-1} is the prefactor of the diffusivity, $l \sim 10$ μm is the rolled sample thickness, and A is the atomic fraction of traps. Unfortunately, the atomic fraction of all vacancy traps is not well known in our experiment. For the atomic fraction of C sites alone, $A \sim 10^{-9}$, one obtains $E^B \sim 0.66$ eV. Assuming other unidentified impurities in the Ni host capture vacancies and form traps with density $A \sim 10^{-6}$ (a not unreasonable figure), one obtains $E^B \sim 0.5$ eV. Given our limited knowledge of the trap density, we conclude that the binding enthalpy is less than ~ 0.66 eV, and is not necessarily inconsistent with ~ 0.5 eV obtained in the deuterium release studies. Thus it is not necessary to invoke a chemical affinity of H for the In probe. Finally, our finding that the binding enthalpies of H and D are equal is unaltered by these considerations.

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[1] J. K. Nørskov, F. Besenbacher, J. Bøttiger, B. B. Nielsen, and A. A. Pisarev, Phys. Rev. Lett. **49**, 1420 (1982); F. Besenbacher, S. M. Myers, and J. K. Nørskov, Nucl. Instrum. Methods Phys. Res., Sect. B **7/8**, 55 (1985).

[2] F. Besenbacher, J. Bøttiger, and S. M. Myers, J. Appl. Phys. **53**, 3536 (1982).

[3] E. Recknagel, G. Schatz, and Th. Wichert, in *Hyperfine Interactions of Radioactive Nuclei,* edited by J. Christiansen, Topics in Current Physics, Vol. 31 (Springer, Berlin, 1983), p. 133.

[4] F. Pleiter and C. Hohenemser, Phys. Rev. B **25**, 106 (1982).

[5] C. Hohenemser, A. R. Arends, H. de Waard, H. G. Devare, F. Pleiter, and S. A. Drentje, Hyperfine Interact. **3**, 297 (1977).

[6] C. Allard, G. S. Collins, and C. Hohenemser, Phys. Rev. B **32**, 4839 (1985).

[7] A. G. Crocker, M. Doneghan, and K. W. Ingle, Philos. Mag. A **41**, 21 (1980); N. Q. Lam, N. V. Doan, and L. Dagens, J. Phys. F **15**, 799 (1985).

[8] M. L. Swanson and L. M. Howe, Nucl. Instrum. Methods Phys. Res. **218**, 613 (1983).

[9] G. S. Collins, G. P. Stern, and C. Hohenemser, Phys. Lett. **84A**, 289 (1981); G. S. Collins and R. B. Schuhmann, Hyperfine Interact. **15/16**, 391 (1983).

[10] A. R. Arends, C. Hohenemser, F. Pleiter, H. de Waard, L. Chow, and R. M. Suter, Hyperfine Interact. **8**, 191 (1980).

[11] F. Pleiter, A. R. Arends, and H. G. Devare, Hyperfine Interact. **3**, 87 (1977).

[12] G. S. Collins and R. B. Schuhmann (unpublished).

[13] Saturation of the C_{H} fraction at the initial level of C was clearly observed in other measurements made at 77 K.

[14] It is possible that site M_H arises from decoration of site M. However, the low range of values of ω_0 for M_{H} suggests that quadrupole interactions induced by the H atoms are small. It is then easier to explain the characteristics of site M_{H} via trapping at site C rather than site M.

[15] S. M. Myers, P. Nordlander, F. Besenbacher, and J. K. Nørskov, Phys. Rev. B **33**, 854 (1986).

[16] G. S. Collins, C. Allard, R. B. Schuhmann, and C. Hohenemser, Phys. Rev. B **28**, 2940 (1983).

[17] W. Eichenauer, W. Löser, and H. Witte, Z. Metallkd. **56**, 287 (1965).

[18] L. Katz, M. Guinan, and R. J. Borg, Phys. Rev. B **4**, 330 (1971).

[19] S. T. Picraux, Nucl. Instrum. Methods **182/183**, 413 (1981).

[20] S. M. Myers, S. T. Picraux, and R. E. Stolz, Appl. Phys. Lett. **37**, 168 (1980).

[21] A. McNabb and P. K. Foster, Trans. Metall. Soc. AIME **227**, 618 (1963).