mirror-confined plasmas.

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Hydrogen Tunneling States in Niobium*

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The known low-temperature properties of H and D in Nb are explained by a model of tunnel-split pocket states.

The structure and diffusive properties of H centers in metals have recently become the focus of renewed interest due in part to the nonclassical nature of several observed properties. Even for the best-studied case of dilute solutions of H in Nb, however, the local structure of the H impurity has remained a puzzle. In this Letter we show that the known properties of H and D in Nb possess a consistent and satisfactory interpretation in terms of a system of tunnel-split pocket states.

Our discussion employs octahedral (o), tetrahedral (t), and triangular (τ) interstitial sites of the bcc lattice, distinguished by differing symbols in Fig. 1(a). H diffuses by hopping even at low temperatures[1]; it therefore seems probable that self-trapping localizes these impurities. For this reason we suppose that a H wave function centered on one site may spread onto *dissimilar* neighboring sites only. Figures 1(b)–1(d) show the octahedral-, tetrahedral-, and triangular-centered orbital systems that follow from these assumptions. In the remainder of this Letter we examine the consequences of these ideas for the specific case of H and D in Nb.

The observations to be explained are as follows: (a) Large deviations from a harmonic Debye-Waller broadening appear in neutron quasielastic-scattering results,[2,3] which can be analyzed as the sum of *two* rms amplitudes, ~0.14 and ~1 Å, respectively. (b) Heat-capacity[4] and thermal-resistance[5] anomalies occurring in Nb-H and Nb-D dilute solutions at ~1°K exhibit marked nonclassical isotope effects. (c) Neutron structure analysis[6] and diffuse scattering[7] have

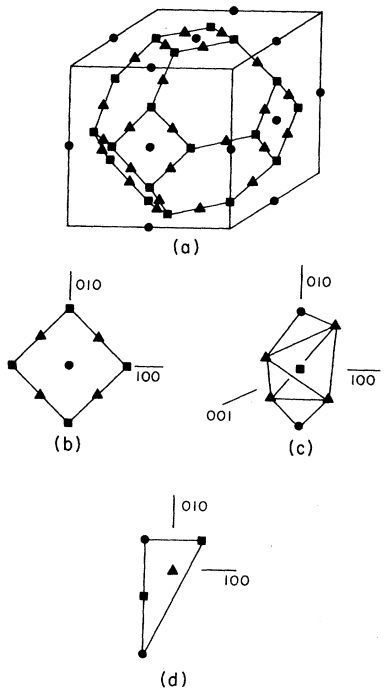

FIG. 1. (a) Geometry of interstitial sites in the bcc lattice showing octahedral (●), tetrahedral (■), and triangular (▲) sites. Orbital systems for o-, t-, and τ-centered tunneling levels are shown in (b), (c), and (d). The o sites are not occupied in Nb.

established that t sites are occupied and that τ sites have occupation probabilities similar to t sites, at least at room temperature, but that o sites have at most a very minor occupancy. (d) Elastic constant[8] and neutron[9] and diffuse x-ray[10] scattering results show that the H (D) solutes cause lattice distortions possessing approximately cubic symmetry. A delocalized solute model has been suggested[2,8,11] to rationalize these results.

We can satisfy all neutron-scattering requirements by models 1(b)–1(d) with the added constraint that o sites in Nb are strongly repulsive and therefore not occupied. The 0.14-Å Debye-Waller factor then compares well with the value (0.12 Å) expected for a harmonic oscillator with the observed proton energy,[12,13] while the mean ring radius of 0.7 Å in model 1(b) gives the larger width contribution. We presume that the observed high-temperature effect[2,3] represents an activated delocalization, and that a tunneling delocalization from reduced contact with the host phonon bath occurs only at low temperatures. The models 1(c) and 1(d) lacking o sites may be less satisfactory, with tetrahedron corners at a radius 0.58 Å in 1(c) and the same distance as a linear dimension in 1(d). We return later to the fact that all alternatives lack exact cubic symmetry.

To treat these models in detail we attribute diagonal energies ϵ and 0 to t and τ sites, respectively, and an off-diagonal hopping integral V to the $t \leftrightarrow \tau$ transition.[14] Upon diagonalization of the 8×8 matrix one obtains for the octahedral case [model 1(b)][15]

$$E_1, E_8 = 2V[w \mp (w^2+1)^{1/2}], \tag{1a}$$

$$E_{2,3}, E_{6,7} = 2V[w \mp (w^2+\tfrac{1}{2})^{1/2}], \tag{1b}$$

$$E_4 = 0, \quad E_5 = 4Vw. \tag{1c}$$

Similarly, the tetrahedral case [model 1(c)] gives

$$E_1, E_5 = 2V[w \mp (w^2=1)^{1/2}], \tag{2a}$$

$$E_{2,3,4} = 0, \tag{2b}$$

and the triangular case [model 1(d)] results in

$$E_1, E_3 = 2V[w \mp (w^2+\tfrac{1}{2})^{1/2}], \tag{3a}$$

$$E_2 = 0, \tag{3b}$$

where $w = \epsilon/4V$. The specific heat follows from these diagonal energies as

$$C = d\{kT^2(d/dT)[\ln\textstyle\sum_i \exp(-E_i/kT)]\}/dT, \tag{4}$$

in which the sum extends over all states i. None of the results for the models of Figs. 1(b)–1(d) closely resembles the observed C for D in Nb, although 1(b) holds most promise and will be used in what follows. Its eight energy levels are shown as functions of w in Fig. 2.

The two doublets $E_{2,3}$ and $E_{6,7}$ comprise an important aspect of the level scheme in Fig. 2. Both couple to lattice tetragonalities and deform in first order to produce a Jahn-Teller–like static splitting; further splittings result from interactions with random lattice strains (introduced, for example, by hydride precipitation). Lacking coupling constants and experimentally determined strain-field distributions we cannot calculate these effects precisely. To proceed in the absence of detailed information we assume that there exists a uniform distribution of doublet splittings from 0 to αV_D with V_D the deuteron hopping integral. For roughly equal volumes of solution[10] the H and D strain splitting should be nearly identical. However, their tunnel splittings clearly differ, and we shall measure this isotope effect by a factor $\beta = V_H/V_D$.

Figure 3 shows the predicted H and D heat capacities for $w = 0$, relative to their values at the

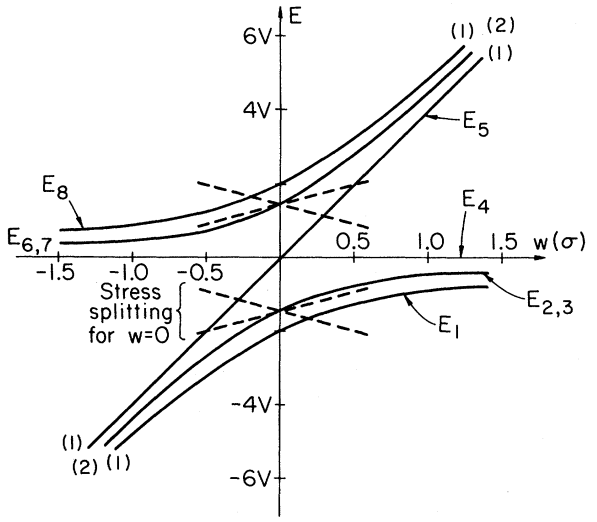

FIG. 2. Tunneling levels of o-centered orbital systems are shown for a fixed V as a function of $w=\epsilon/4V$ where ϵ is the diagonal energy difference between t and τ sites and V is the hopping integral.

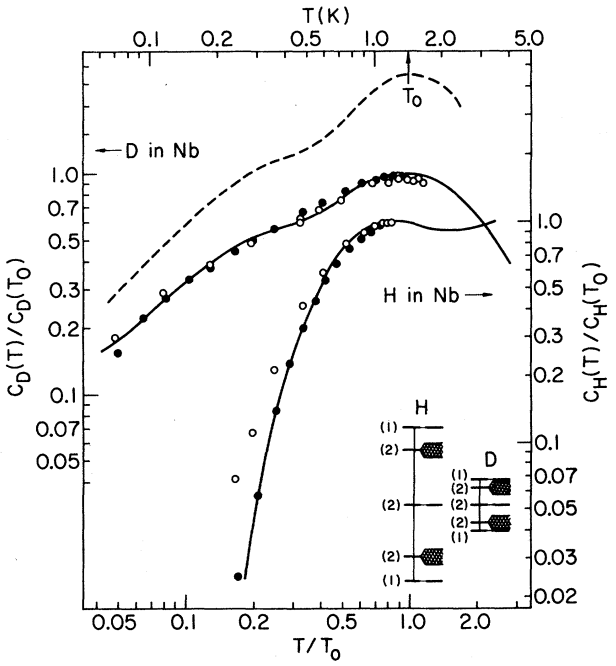

FIG. 3. Experimental heat capacities are shown as a function of temperature for H and D in Nb according to Ref. 4. H data points are for as-received (low-concentration) specimens (●) and for 3000-ppm (atomic) (○). The solid lines represent Eq. (4) for the o-centered tunneling model with $\alpha=0.5$ and $\beta=3$. The broken line represents the D calculation for $\alpha=1.5$ and $\beta=3$ (the curve is displaced vertically for clarity). The H and D level spectra are shown at the lower right.

D-peak temperature $T_0=142$°K, fitted to the experimental results of Sellers, Anderson, and Birnbaum.[4] The two adjustable parameters have values $\beta=3$ and $\alpha=0.5$. This excellent fit is insensitive to w near $w=0$ and is not strongly dependent on α. The broken line in Fig. 3 shows that $C_D(T)$ remains reasonably satisfactory for $\alpha=1.5$ but, since $C_H(T)$ then resembles the $\alpha=0.5$ D result, the composite fit for H and D together is most satisfactory for $\alpha\simeq 0.5$. Splittings for this case are shown at the lower right of Fig. 3. The effect of strain splitting can be seen in the experimental $C_H(T)$ data (Fig. 3) by comparing the low-H-concentration as-received specimen with the specimen containing 3000-ppm (atomic) H and hence a much greater amount of hydride precipitation and strain.

We emphasize that the satisfactory character of the specific-heat predictions follow from three features of the model: (a) the occurrence of a degenerate multiplet as the first excited state with (b) a strain splitting spectrum that spreads back close to the ground state for D but not H (because of the isotope effect in V), and (c) a substantial complex of still higher-lying states (the observed C_D shows the D entropy to be only half-developed at ~0.7°K). These are indeed the salient features of the octahedral tunnel-split model, 1(b). It is possible, but perhaps not likely, that the alternative tunnel-split systems 1(c) and 1(d) could reproduce the observed results with a suitable choice of strain splittings.

It is important to note further that the *magnitude* of the observed effects can be reproduced semiquantitatively by the tunneling model. From an exact diagonalization of the two-well tunnel system one estimates[16]

$$V\simeq\hbar\omega_0(\delta/\pi)^{1/2}\exp(-\delta), \tag{5}$$

with

$$\delta=Md^2(\hbar\omega_0)/4\hbar^2. \tag{6}$$

Here, ω_0 is the H (D) local-mode frequency, M its mass, and $d=0.583$ Å is the $t\rightarrow\tau$ site separation. The theoretical $C(T)$ first peaks at $\sim V/10k$ so, with $\hbar\omega_{OH}\simeq 0.18$ eV, substantial specific heats are expected at 5.6°K for H and 1.2°K for D. These are very satisfactory estimates. The somewhat smaller observed temperatures may well arise from the dressing of hydrogen motion by lattice displacements. In addition, the predicted isotope effect of 4–5 seems in reasonable accord with the observed result $\beta=3$.

By way of contrast, an alternative ascription

of the specific heat to an incoherent hopping redistribution of isotopes over available sites encounters difficulty. Its temperature dependence arises solely through the occupation probabilities $p_j \sim \exp(-\epsilon_j/kT)$ of various sites with energies ϵ_j, and all the specific-heat data must be attributed to a fortuitous distribution of the ϵ_j and their isotope effects. Thus, the tunnel-split model presents a most attractive alternative. We point out that new neutron measurements at low temperatures, and new specific-heat results on strain-free samples (perhaps with much lower hydrogen concentrations), could greatly clarify the structure of the existing tunnel-split centers.

A final point to which we now return concerns the symmetry of lattice strain near hydrogen trapped in Nb interstices. None of the models 1(b)–1(d) is truly cubic, but both 1(b) and 1(c) are nearly so, as will be demonstrated for the case of 1(b). The strain field of a tetrahedral interstitial at $(\frac{1}{2}, \frac{1}{4}, 0)$ is diagonal in the frame of the crystal axes, with principal components of relative size $\epsilon_1{}^t$, $\epsilon_1{}^t$, and $\epsilon_3{}^t$. The triangular sites at $(\frac{3}{8}, 0, \frac{3}{8})$ give different strains of symmetry

$$\frac{1}{2}\begin{bmatrix} (\epsilon_1{}^\tau + \epsilon_3{}^\tau) & 0 & (\epsilon_1{}^\tau - \epsilon_3{}^\tau) \\ 0 & 2\epsilon_3{}^\tau & 0 \\ (\epsilon_1{}^\tau - \epsilon_3{}^\tau) & 0 & (\epsilon_1{}^\tau + \epsilon_3{}^\tau) \end{bmatrix}, \tag{7}$$

in this coordinate system, with $\epsilon_1{}^\tau$ and $\epsilon_3{}^\tau$ the principal τ strains in its own local symmetry system. On summing over all t and τ sites in the octahedral ring one obtains the mean strain field

$$\bar{\epsilon} = \tfrac{1}{2}(\epsilon_3{}^t + \epsilon_3{}^\tau)\begin{bmatrix} 1+e & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+e \end{bmatrix}. \tag{8}$$

in which

$$e = (\epsilon^t - \epsilon^\tau)/2(\epsilon_3{}^t + \epsilon_3{}^\tau), \tag{9}$$

and

$$\epsilon^t = \epsilon_1{}^t - \epsilon_3{}^t, \quad \epsilon^\tau = \epsilon_3{}^\tau - \epsilon_1{}^\tau. \tag{10}$$

The signs of terms in Eq. (10) are determined by the displacements of a hard-sphere model which indicate that ϵ^t and ϵ^τ are both positive, and e in Eq. (9) is therefore probably quite small with respect to unity. The strain field of the octahedral ring may therefore be rather isotropic, in accord with the experimental evidence.[8-10] We presume that such strain fields are associated with H self-trapping in a particular system of tunnel-split orbitals and that diffusion proceeds by hopping to one of the neighboring systems.

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[14]The complete problem, including o sites also, requires diagonal o-site energies ϵ' and their hopping integrals V', V'', to t and τ sites. The model excluding o sites was chosen in conformity to the neutron-scattering results.

[15]In the equations with ambiguous signs, the first quantity on the left corresponds to the upper sign on the right.

[16]See, e.g., E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1961).