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Quasimolecular Jahn-Teller resonance states in the bcc metallic hydrides of vanadium, niobium, and tantalum

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The unusual properties of the group Vb bcc hydrides are shown to derive from a particular d-band quasimolecular resonance state localized near interstitial hydrogen. This state is schematically shown to be grounded in fundamentals. The point of departure is an Anderson-Newns approach to the problem of a single hydrogen atom in a transition metal, with the metal states in a mixed nearly-free-electron-tight-binding representation. Orthogonalization of pseudo-plane-wave states to the hydrogen $1s$ "core" state leads to a Hamiltonian with site-diagonal disorder (Anderson Hamiltonian) for the d band. This gives the possibility of induced, localized d states. Assuming that localized electron states derived from the d band exist and are confined to the shell of metal atoms nearest the impurity, symmetrized linear combinations of atomic orbitals (-molecular orbitals) (LCAO-MO) are constructed for impurity polyhedra in the group Vb metals. The orientation of atomic d orbitals used for this construction is that of the pure metal. One of the MO's so obtained is shown to be particularly well suited, in terms of availability and closeness to the Fermi level, for screening purposes. This state is degenerate and, by analogy with other well-known states (e.g., impurity-vacancy pairs in Si), should have a strong Jahn-Teller interaction. A particularly simple $\langle 111 \rangle$ distortion proves to be key for understanding previously unexplained properties in the Vb metal-hydrogen systems, viz. cubic lattice distortion, hydrogen diffusion, and excess partial entropy. Following an argument that the Jahn-Teller distorted state should persist at higher concentrations because of its essentially molecular character, a blocking rule is formulated based on the assumed integrity of this state. The rule is shown to explain hydrogen partial entropy versus concentration, including a sharp decrease in entropy near $[H]/[M] = 1$. It also predicts that hydrogen diffusion should become increasingly correlated at higher concentrations, agreeing with a recent experiment. Finally, exceptions to the blocking rule are discussed in terms of an additional Jahn-Teller state, and it is shown that observed superlattice structures can be understood in terms of one or the other of the two Jahn-Teller states.

I. INTRODUCTION

The hyrides of V, Nb, and Ta are among the best characterized of all transition-metal hyrides, but yet they are not understood—particularly regarding the connection between observed properties and electronic structure. This paper attempts to close that gap by showing that much of the observed behavior derives straightforwardly from a particular d-band resonance state localized on the shell of metal atoms immediately adjacent to interstitial hydrogen. Further, this quasimolecular resonance state is shown to be fundamentally grounded. To establish a suitable frame of reference, the argument must begin with a brief discussion of important properties[1] that accentuates puzzling features.

The phase diagrams of the group-Vb hydrides have been extensively charted; most prominently through classical pressure-volume-temperature (P-V-T) techniques, resistivity determinations, and magnetic susceptibility measurements. Structural details have been largely worked out through the complementary techniques of x-ray and neutron diffraction, and also through the use of transmission electron microscopy. Dynamical features such as acoustic and optical (hydrogen) modes and hydrogen diffusivities have been studied by quasielastic and inelastic neutron scattering, by NMR, and by other more specialized techniques.

An important dynamical earmark is the existence of hydrogen optical modes with frequencies well above the highest lattice (acoustic) frequencies.[1(a)] Detailed study of these modes reveal that the interstitial hydrogen atoms behave as an assemblage of Einstein oscillators. There are also a number of important thermodynamic and structural features. Thus, at sufficiently high temperatures ($\gtrsim 500$ K), the Vb hydrides form a continuous solid solution phase[2] up to $C_H \simeq 1$ ($C_H \equiv H/M$). The metal sublattice retains the bcc structure throughout, and the hydrogen atoms almost randomly occupy tetrahedral interstitial sites (t sites), of which there are six for every M atom (Fig. 1). At lower temperatures, there is a great variety of hydride phases,[1(b)] in which hydrogen atoms order among themselves. These orderings take place on a sublattice of t sites, but in V there is also ordering on a sublattice of octahedral interstitial sites. Apart from these special cases in V, the metal sublattice in ordered hydride phases is pseudocubic, showing very small distortions from the parent metal bcc structure.

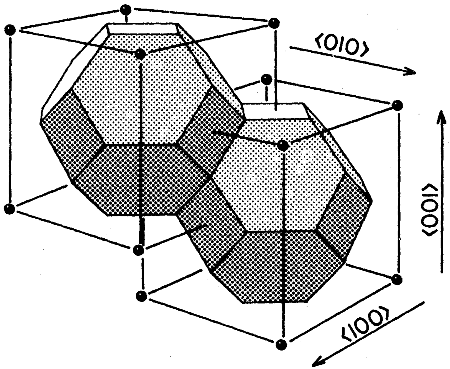

FIG. 1. bcc lattice with tetrahedral interstitial sites (*t* sites) located by corners of the truncated octahedra.

Indeed, most of the important properties characteristic of the parent metal (e.g., phonon spectra,[1(a)] electronic properties[1(c)]) are not greatly modified by the presence of hydrogen for $C_H \lesssim 1$. For higher hydrogen concentrations the metal sublattice undergoes a first-order structural transition, but we are not concerned with these higher hydrides.

The interactions responsible for formation of ordered hydride (superlattice) phases in the Vb metals are not understood. In fact, more than a few of the important properties of these metal-hydrogen systems have not been explained or, at best, are only poorly understood. One of these is hydrogen diffusion, which has been perhaps the most intensively studied property, both experimentally and theoretically. A variety of ideas have recently been advanced to explain hydrogen diffusion in the Vb metals.[1(d),3,4] They share the common assumption that valence electrons need be considered only in a gross, averaged sense as potential energy surfaces for nuclear motion and can otherwise be ignored. But in spite of these efforts, some outstanding questions remain unanswered. Thus, while proton diffusion is known to be phonon limited,[1(d)] the absolute magnitude (at 300 K, comparable to proton migration in liquid H_2O) is difficult to understand in terms of obvious polaronic concepts.[4] Furthermore, quasielastic-neutron-scattering studies, which had been so successful in the microscopic elucidation of proton diffusion in Pd hydride,[5] have baffled all attempts at description for the Vb hydrides.[6]

Stoneham[4] has argued that these difficulties can be resolved in terms of a model that has the proton tunneling (in the coherent sense) among a small group of sites and occasionally hopping from one group to another. This model, though, has not been developed quantitatively, nor has any basis been offered for such bimodality. Nonetheless, there is experimental evidence at low temperatures that hydrogen in Nb doped with oxygen does indeed tunnel among a small group of sites.[7] It is unclear whether oxygen merely inhibits formation of an ordered hydride phase or, instead, forms a complex with hydrogen. If it is the former, Stoneham's concept merits added attention.

Another puzzling hydride property—one that has not received much notice—is the observation of anomalously large hydrogen partial entropies in the limit of small C_H for temperatures near 700 K.[8] At lower temperatures this quantity has not been adequately characterized; experimental difficulties have apparently limited its determination to one or two investigations.[9] Even so, these latter observations (which do not show an anomaly) have been cited[8(a)] in support of the conventional description, whose base state has hydrogen localized in deep potential wells on individual *t* sites.

But of all the puzzling features, the outstanding anomaly is the well-established observation that the tensor characterizing distortion of the metal sublattice near the proton is (apart from experimental uncertainty) cubic[1(e)]—this in spite of the tetragonal symmetry of the *t* site. Contrasting sharply with the cubic lattice distortion is a clearly observed anisotropy for the optical modes.[1(a)] The anisotropy is quantitatively predicted by local symmetry on a model with central forces between proton and nearest metal atoms only.[10] Taken together, these two disparate facts suggest that the force fields determining local modes on the one hand and lattice distortion on the other are *distinct*. Indeed this idea is implicit in a recent study in which M-H and M-M force constants (including only the four M atoms nearest to the impurity) were adjusted in a lattice-dynamical calculation to give agreement with observed local mode frequencies, lattice distortions, and elastic constants.[11] A good fit was obtained, but derived M-M force constants were greatly altered relative to pure-host-metal values. Such an effect might be plausible in terms of an induced electronic state (e.g., a screening state) localized on the nearest shell of metal atoms, but the existence of *a cubic* lattice distortion near the proton must be seen as an *accidental* feature of that concept.

This brings us to a basic difficulty—not only for the Vb hydrides, but for all transition-metal hydrides—that seriously hampers progress toward a full appreciation of hydride properties such as those described above, namely, what is the electronic character near interstitial hydrogen in the limit of infinite dilution? In view of the observed continuity of properties between the dilute limit and the maximum hydrogen concentrations attainable, this is surely a question of fundamental significance for the Vb bcc metal hydrides. Friedel[12] has given a brief, qualitative discussion of a single hydrogen atom in a transition metal. His approach emphasizes the *protonic* character of the impurity. The work of Newns[13] describing hydrogen chemisorption is more directly relevant, though, primarily because the *atomic* character of hydrogen is emphasized at the outset. Chemisorption is a surface problem, but there are significant reasons for believing it to be not altogether different from a bulk solution of hydrogen.[14]

In the following sections we show that for hydrogen in the bulk, Newns' approach for chemisorption, plus inclusion of certain orthogonality terms, leads naturally to an Anderson Hamiltonian with site-diagonal disorder[15,16] for the d-band states. This gives the possibility of localized electronic states derived from the d band. We do not attempt a direct solution of this problem, but instead proceed on the assumption that for a localized d state to play a role in the screening process, it must (i) be describable as a sum over d-band states which are not already occupied in the pure metal; (ii) have a mean energy reasonably close to the Fermi level; and (iii) be primarily confined to the nearest shell of metal atoms about the impurity.

Using an LCAO-MO approach, we construct properly symmetrized one-electron states confined to the nearest shell. The atomic basis consists of d orbitals whose orientation is as for the pure metal. The set of states so obtained are approximately related to the Fermi level (E_F) of the Vb metals by comparing the molecular bonding character of these states with the known character of the d band in bcc metals. Only one of these states matches the criteria of availability and closeness to E_F. An important feature of this state is the existence of spatial degeneracy. After comparing this quasimolecular system with certain well-studied systems, we argue that a strong Jahn-Teller (JT) interaction is likely, and that distortion along $\langle 111\rangle$ bonds is the expected mode of stabilization. We show that a simple static displacement along a single $\langle 111\rangle$ bond gives the cubic lattice distortion and at the same time suggests a remarkable mechanism for diffusion, not unlike that postulated by Stoneham.[4] Furthermore, this description explains immediately the excess partial entropy. Then we formulate a simple blocking rule for neighboring impurity atoms, based on intuitive ideas about the molecular character of the induced state together with certain experimental facts. Finally, we show that much of what is known about the Vb bcc hydrides at higher concentrations can be rationalized in terms of this rule.

In short, the model set forth in this article—while highly schematic—attempts to unify a large body of facts about H in the Vb metals under a description that is grounded (at least tentatively) in fundamental principles of solid-state electron physics, but that retains, almost paradoxically, molecular simplicity.

II. HYDROGEN SCREENING–THE EFFECT OF ORTHOGONALIZATION

This section gives a schematic treatment of the problem of a single interstitial hydrogen impurity in transition metals, patterned on the model used by Newns[13] to describe hydrogen chemisorption. An important difference is the inclusion here of orthogonalization effects on metal conduction states. The role of this additional perturbation is most clearly seen by describing the pure metal in a mixed tight-binding and pseudopotential representation.[17] Specifically, we argue that orthogonalization of pseudo-plane-wave states induces site-diagonal disorder in the tight-binding Hamiltonian.

The chemisorption model of Newns follows closely Anderson's description of magnetic impurities in alloys,[18] which treats the effect of the solute atom entirely as that of a separate localized state rather than as an impurity potential acting on the free-electron gas. According to Anderson,[18] the essential criteria for validity of the model are (i) the "inner-shell" orbital must be very different from free-electron states of the solvent, and (ii) it must be sufficiently localized so that its Coulomb self-energy integral is not screened out. Generally speaking, these conditions should be satisfied by interstitial hydrogen in transition metals; nevertheless, the 1s state is likely to have appreciable band character, especially in regions not too close to the proton. We consider this to be a significant perturbation that should be explicitly included at the outset in the application of Anderson's model to interstitial hydrogen.

The single impurity is represented by the neutral hydrogen atom and the total representation (metal plus hydrogen) is given below in block form:

$$\begin{matrix} 1s\text{-}1s & 1s\text{-}c & 1s\text{-}d \\ c\text{-}1s & c\text{-}c & c\text{-}d \\ d\text{-}1s & d\text{-}c & d\text{-}d \end{matrix} \quad , \tag{1}$$

where the c and d blocks correspond to pseudo-plane-wave states and tight-binding states, respectively. Just as for the tight-binding states in Mueller's treatment,[17] the hydrogen 1*s* state is considered at first as part of the core and, in the spirit of the orthogonalized-plane-wave approximation,[19] all pseudo-plane-wave states must be made orthogonal to the 1*s* state. (This is similar to Bennemann's treatment[20] for point defects in covalent crystals.) Clearly, only those states having A_1 symmetry about the impurity site can be affected. In terms of unperturbed pseudo-plane-wave conduction-band states $\psi_{\vec{k}}$ (orthogonalization terms caused by the *d* states[17] are implicitly included in the definition of $\psi_{\vec{k}}$), the modified states in the presence of the impurity are

$$\phi_{\vec{k}} = \psi_{\vec{k}} - [M_s(\vec{k})\psi_{1s}]C^{-1}\,, \tag{2}$$

where the normalizing factor C is given by

$$|C|^2 = 1 - |M_s(\vec{k})|^2\,, \tag{3a}$$

$$M_s(\vec{k}) \equiv \int \psi_{\vec{k}}^* \psi_{1s}\, d\tau\,. \tag{3b}$$

At this level, the effect of orthogonalization is a redistribution of electron density within the conduction band—depletion of charge density in the vicinity of the impurity is offset by a corresponding increase delocalized over the crystal. But this changes the effective potential in the vicinity of the impurity, introducing an attractive Coulombic interaction through the one-electron Hartree potential, localized around the impurity. In the Hartree-Fock (HF) approximation, electrons in tight-binding states "see" an effective electrostatic potential associated with occupied conduction-band states, which for the pure metal is

$$V_{\mathrm{HF}}^{c}(\vec{r}_1) = 2 \sum_k \int |\psi_k(\vec{r}_2)|^2 r_{12}^{-1}\, d^3 r_2\,. \tag{4}$$

In the presence of a single hydrogen impurity, this effective potential is modified by the orthogonalization of conduction states given by Eq. (2). To first order in the overlap M_s, the change in the effective potential [obtained by substituting Eq. (2) into Eq. (4)] is

$$V_{\mathrm{or}}(\vec{r}_1) = -2 \sum_k M_s(\vec{k}) \int (\psi_k^* \psi_{1s} + \mathrm{C.C.}) r_{12}^{-1}\, d^3 r_2\,. \tag{5}$$

This attractive interaction lowers the energy of the 1*s* state and *also of tight-binding orbitals on nearest-neighbor metal atoms*. The reason for choosing the Mueller representation[17] should now be transparent. For H_{dd} of Eq. (1), we write

$$\mathrm{H}_{dd} = \sum_n |\mu n\rangle \epsilon_{\mu n} \langle \mu n| + \sum_{\substack{n \neq n' \\ \mu,\mu'}} |\mu n\rangle t_{\mu n,\mu' n'} \langle \mu' n'|\,, \tag{6}$$

where $|\mu n\rangle$ is an atomic *d* function centered on site *n*, and μ describes orbital symmetry. The one-electron orbital energies $\epsilon_{\mu n}$ are site independent in the pure metal. The interstitial hydrogen impurity, through the effect of orthogonalization on conduction states and thereby on the Hartree one-electron potential, produces site disorder in the $\epsilon_{\mu n}$. If off-diagonal terms $t_{\mu n,\mu' n'}$ are unaffected, then Eq. (6) for the impurity problem is just the Anderson Hamiltonian for site-diagonal disorder.[15] An unusual feature in the present case is that metal atoms are affected in groups of four (assuming that only nearest-neighbor metal atoms see V_{or}). The point to be emphasized here is the possibility of *localized electronic states* (virtual or real) derived from the *d* band. A variety of localization effects have been determined for this Hamiltonian, mostly through application of the coherent-potential approximation (CPA) method,[21] both to model systems[16] and to real systems.[22]

In the present case, the system can apparently respond to V_{or} in two distinct ways: transfer of electrons from the conduction band to either the 1*s* state or to a state derived from the *d* band and localized primarily on the shell of metal atoms nearest the impurity. The response will be determined by the important parameters of the problem, namely, (i) the net electron density depleted from the vicinity of the impurity by orthogonalization; (ii) the energy of available localized *d* states relative to E_F; (iii) the importance of the Coulomb self-repulsion integral (U) for the 1*s* state relative to that for the localized *d* state. The latter effect clearly favors formation of a localized *d* state (localized on a crystal scale, but delocalized on a molecular scale).

If the various parameters can be determined and the conduction bands reasonably modeled, it should be possible to obtain a self-consistent solution in the Hartree-Fock approximation. The essential features of the self-consistency problem appear to be (i) interaction of the 1*s* state with orthogonalized band states along with a large repulsive Coulomb interaction between two electrons in the 1*s* orbital, and (ii) interaction with band states of a state derived from the *d* band in which electron density is shared by metal atoms in the shell nearest the impurity. For the latter state, U is probably unimportant because of conduction-band screening effects.

The first part of this problem is essentially that considered by Newns,[13] but with appropriate modifications for the bulk. The parameters are expected to be roughly comparable to corresponding ones for the chemisorption problem.[14] The coupling integral is perhaps greater in the bulk, simply because of a greater number of metal atoms near the impurity (this advantage may be offset somewhat by the role of dangling d orbitals on the surface). Thus, as in the case of hydrogen chemisorption,[13] a nonmagnetic solution for the 1s bound state is also likely in the bulk. Furthermore, this state should lie below the d band, with no density at the Fermi level. A localized d-band screening state, on the other hand, would necessarily lie near E_F.

III. LCAO-MO DESCRITPION OF INDUCED *d* STATE

In this section, the foregoing ideas are applied to the particular problem of hydrogen in the Vb metals. The primary aim here is the evocation of a spatially degenerate d state and thereby the possibility of a stabilizing Jahn-Teller distortion.[23] We do not attempt a self-consistent solution, nor are we directly interested in the 1s impurity state. Instead, the discussion focuses on description of possible localized d states using LCAO-MO theory, in which only d orbitals on the four metal atoms nearest the impurity are considered. Because such a state (if it exists) must derive from the metal d band, atomic orbitals describing this state are determined by the nature of the d band. In bcc metals the d band is known to be sharply divided into bonding and antibonding halves of nearly equal weight.[24] According to Friedel,[24(a)] this is due to the fact that all the d functions can be chosen with their lobes pointing to first- or second-nearest neighbors.

The atomic basis set shown in Fig. 2 has been chosen to satisfy the preceding specification with lobes of t_{2g} functions [Fig. 2(a)] approximately along ⟨111⟩ directions, while e_g lobes [Fig. 2(b)] are along ⟨100⟩ directions. Only two d orbitals per metal atom are included with the assumption that the remaining three d orbitals are significantly less stabilized by V_{or} than those of Fig. 2. Qualitatively, this assumption is justified by the expectation that V_{or}, with its r_{ij}^{-1} weighting factor, is localized entirely within the shell of nearest-neighbor metal atoms. A second, perhaps more significant reason, is the fact that the states made up of the neglected d functions have primarily *atomic* character as opposed to molecular or delocalized character of important states based on the d functions of Fig. 2. Screening of the repulsive Coulomb self-energy integral will be less complete for states with atomic character than for those having some delocalization.

The quasimolecule shown in Fig. 2 belongs to the D_{2d} point group. A set of symmetrized MO's corresponding to the atomic basis of Fig. 2 can be derived by inspection and are shown in Table I along with their irreducible representations and bonding character. This latter property refers to the nodal character of the MO along the ⟨100⟩ and ⟨111⟩ bonding directions; it is not unlike the corresponding feature of extended d states which, for bcc metals, places these states in either the bonding or antibonding half of the d band. In fact, the molecular states of Table I can be considered as prototypes of the d band in the spirit of cluster calculations applied to transition metals.[14] Thus, we argue that the bonding character of the MO's in Table I qualitatively determines their location relative to E_F. The valence electron configuration for the Vb metals is d^4s^1, so that E_F falls in the bonding half of the d band, just short of the pro-

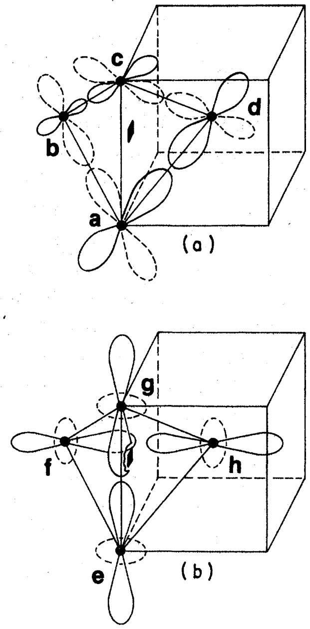

FIG. 2. Atomic basis for the D_{2d} four-atom metal impurity polyhedron: (a) t_{2g} orbitals; (b) e_g orbitals. The distorted square represents hydrogen on a t site. Solid and dashed lobes have opposite phases.

TABLE I. Symmetrized MO's based on atomic orbitals of Fig. 2.

State	Atomic orbital description	Bonding character
$\psi_t(B_1)$	$\vert a\rangle + \vert b\rangle + \vert c\rangle + \vert d\rangle$	Bonding
$\psi_t(E)$	$\vert a\rangle \pm \vert b\rangle - \vert c\rangle \mp \vert d\rangle$	Nonbonding
$\Psi_t(A_2)$	$\vert a\rangle - \vert b\rangle + \vert c\rangle - \vert d\rangle$	Antibonding
$\Psi_e(A_1)$	$\vert e\rangle + \vert f\rangle + \vert g\rangle + \vert h\rangle$	Bonding
$\Psi_e(B_2)$	$\vert e\rangle + \vert g\rangle - \vert f\rangle - \vert h\rangle$	Bonding
$\Psi_e(E)$	$\vert e\rangle - \vert g\rangle \pm \vert f\rangle \mp \vert h\rangle$	Antibonding

nounced minimum separating the two halves. Therefore, the *bonding* states of Table I are related to states which are, for the most part, already occupied in the pure metal and are thus unavailable. The *antibonding* states, on the other hand, lie well above E_F and are not likely to be important. That leaves the nonbonding state $\psi_t(E)$, which can reasonably be placed right at the minimum, several eV above E_F (the attractive term V_{or} will bring it still closer). This state is schematically depicted in Fig. 3(a) as a resonance or virtual bound state superimposed on the d-band density of states, and is also shown as a combination of t_{2g} orbitals with two bonds and two nodes along $\langle 111\rangle$ directions. The striping represents conduction-band states.

In zeroth order, $\psi_t(E)$ is doubly degenerate [a distinct electron state results when bonds and nodes in the MO of Fig. 3(a) are interchanged]. This fact, together with the proximity of E_F, means that if $\psi_t(E)$ exists, a stabilizing Jahn-Teller (JT) distortion should be operative—at least in principle. Whether in fact such a distortion occurs is a self-consistency question, but clearly a strong JT effect is required to compete with the nearly 1 eV interaction between localized and band states.[18]

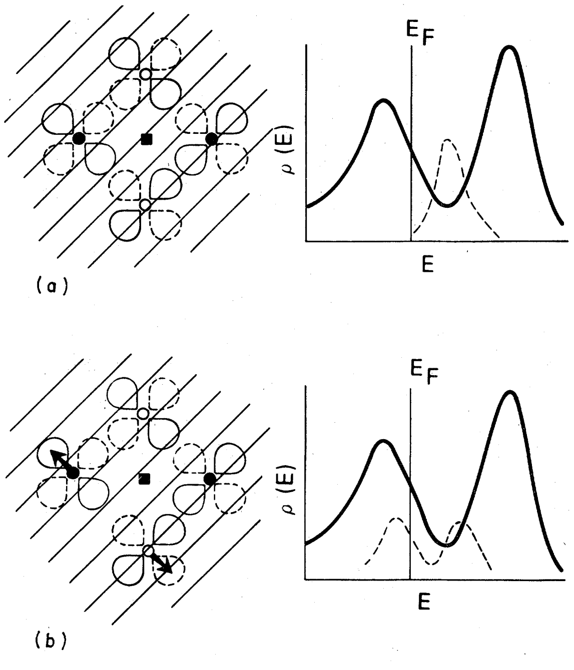

FIG. 3. Schematic of postulated Jahn-Teller distortion: (a) undistorted state [$\psi_t(E)$]; (b) distorted state [ψ_{JT}]. The four-atom quasimolecule is viewed along $\langle 100\rangle$. Filled and open circles represent M atoms at $z=\frac{1}{4}$ and $-\frac{1}{4}$, respectively. The square represents an H atom at $z=0$ (unit of length is the bcc lattice constant a). The striping represents band states. Resonance state and band states are scaled differently in the $\rho(E)$ diagrams.

In order to justify the LCAO-MO approach employed here and at the same time obtain an estimate of the JT interaction, we briefly describe analogous systems whose electronic properties are reasonably well understood. First, there are $M_6X_{12}^{2+}$ halide-metal clusters of Nb and Ta in which the metal atoms are octahedrally arrayed with intermetallic separations nearly the same as for the pure metals.[25] Clusters such as these have recently attracted considerable attention as metal surface analogues.[26] Metal-to-metal bonding of the Nb and Ta clusters has been treated by a simple MO scheme[27] not unlike that employed here for the M_4H impurity cluster. Notably, the lowest bonding MO's have the same σ overlap as that shown in Fig. 2. Electronic spectra of $M_6X_{12}^{2+}$ clusters have been interpreted using the above MO scheme and are consistent with strong sigma bonding.[28] Especially interesting is the assignment of a peak at about 5 eV to a transition between bonding and antibonding states made up of t_{2g} atomic orbitals. The same sort of σ bonding is involved in $\psi_t(E)$ and in the metallic d band itself where the 5–10 eV separation between bonding and antibonding halves measures its strength. Against this backdrop, a strong JT interaction for $\psi_t(E)$ is not unlikely.

Consider now those defects in diamond and silicon, described primarily by Watkins,[29] that have large static JT distortions with stabilization energies of about 1 eV. The silicon[29(a)] defects are various impurity-vacancy pairs and the diamond[29(b)] defects are substitutional nitrogen and the neutral vacancy. Although these defects are not like interstitial hydrogen in bcc metals, there are some important similarities: (i) the analogy between the d band in bcc structures and bonding and antibonding bands in covalent crystals has been noted elsewhere[24(b)]; (ii) simple one-electron descriptions using symmetrized LCAO-MO's localized on small clusters around the defect have qualitatively explained certain EPR observations, particularly so regarding JT distortions.[29(a)] More sophisticated cluster calculations reveal significant delocalization effects (~60% of the vacancy wave function in silicon is localized on the nearest shell) also agreeing with experiment. Even so, the important qualitative features of the simple model are not lost through sophistication. Especially notable is the demonstration that, with only a small amount of delocalization in the solid, many-electron effects are substantially smaller than crystal-field or JT energies.[29(c)]

These cluster and semiconductor results lend support to the present LCAO-MO description of

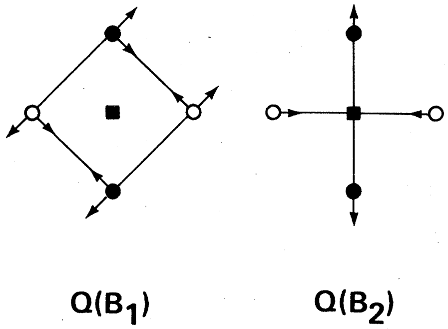

FIG. 4. Jahn-Teller active vibrational modes for the four-atom quasimolecule. View is same as in Fig. 3. See text for description of internal coordinates.

possible localized d states induced by hydrogen in bcc metals. This is especially so given that we are here primarily interested in qualitative rather than quantitative features. Again, we argue that if an induced d state approximated by $\psi_t(E)$ actually exists, then it is reasonable to expect a stabilizing JT distortion.

Taking the four ⟨111⟩ displacements and the two ⟨100⟩ displacements as internal coordinates[30] for the quasimolecule of Fig. 1, JT active vibrations[31] can be easily derived and are shown in Fig. 4. This figure, when compared with Fig. 3(a), reveals that only the B_1 vibrational mode directly affects $\psi_t(E)$. Considered naively, this predicts system stabilization via a static B_1 distortion. But in cases where the JT interaction is comparable to electronic energies (e.g., defects in irradiated silicon[29(a)]), stabilization is not solely dependent on the behavior of a single electronic state and thus cannot be readily predicted. With this in mind, we treat the particular distortion that stabilizes $\psi_t(E)$ as an unknown, but with the expectation that ⟨111⟩ displacements are involved. Figure 3(b) shows a particularly simple stabilizing distortion in which only two metal atoms are displaced along a ⟨111⟩ bond axis. This distortion is not symmetric with respect to the t site (the center of symmetry), so that the graphic depiction of the stabilized MO cannot be an accurate representation for other than the nodal separation along the distortion axis. The two resonance states energetically split by the distortion are also illustrated in Fig. 3(b). The stabilized resonance state is hereafter referred to as ψ_{JT}.

At this point it is worthwhile to review the primary motivation behind the essentially qualitative approach of Secs. I and II. As noted in the Introduction, the unexpected fact of a cubic lattice distortion around the hydrogen impurity together with the expected tetragonal anisotropy of hydrogen optical modes suggest that *distinct* force fields are operative for these two effects. An induced localized electronic state, having no direct interaction with the impurity state, provides the necessary mechanism. By itself though, this idea cannot explain the observation *for all three* Vb metals of a lattice distortion that is sensibly *cubic*.[1(e)] This key fact strongly hints at existence of some qualitative feature as the determining factor. It is precisely here that the idea of a stabilizing Jahn-Teller distortion has its greatest strength; furthermore, it is here that the highly qualitative approach of the present paper finds justification.

Clearly, if the overall lattice distortion caused by interstitial hydrogen in the Vb metals is dominated by the stabilizing ⟨111⟩ displacement of Fig. 3(b), then the observed cubicity is immediately explained. The hydrogen optical modes, on the other hand, are primarily determined by direct interactions of the impurity state with those metal states totally symmetric about the occupied t site. The effect of the JT distortion on these interactions is second order and small. This, then, reconciles the tetragonal anisotropy of the optical modes with the cubic lattice distortion. In the following sections, we show that the particular distortion depicted in Fig. 3(b), together with the essentially molecular (closed-shell) character of ψ_{JT} are key for understanding the remaining puzzles described in the Introduction. As such, these simple ideas connect the preceding formal description to the observed behavior of hydrogen in the Vb metals.

IV. HYDROGEN DIFFUSION

This section describes certain dynamical effects expected for the proposed resonance state, ψ_{JT}. First of all, Fig. 3(b) shows clearly that four distinct but equivalent ⟨111⟩ distortions are possible for ψ_{JT}. Such orientational degeneracy is usually associated with a dynamic JT effect,[29(a),31] whereby the distortion axis reorients among the equivalent states. Because this motion displaces lattice atoms, it is phonon limited.[31] By itself, this effect is not especially interesting, but there exists the possibility of a separate, competing process. The distortion shown in Fig. 3(b) introduces an interesting topological disorder into the sublattice of t sites. The hexagonal ring of t sites normal to the JT distortion axis (see Fig. 1) has been singled out—the six sites on that ring are mutually equivalent, but distinct from all other sites. The phonon drag that limits motion of hydrogen among these six sites is small (the distortion axis does not move), giving preferential hopping or possibly coherent tunneling[32] on hexagonal rings. Motion of hydrogen to a site on a different ring necessarily implies physical displacement of the distortion axis.

If the hydrogen ring motion is much faster than JT reorientation, then their combined effect gives a striking mechanism for macroscopic diffusion of hydrogen. The electronic state ψ_{JT}, its distortion axis stationary, follows hydrogen adiabatically around the ring defined by that axis. Hydrogen is periodically trapped on individual ring sites by energetic phonons moving through the crystal. At the same time, certain of these phonons activate a JT reorientation. Once that happens, hydrogen whirls about the displaced distortion axis on a new ring, thus pirouetting through the crystal lattice. These ideas are illustrated in Figs. 5 and 6.

When hydrogen is localized on a particular t site within a given ring (also called ring state), there are three distinct JT reorientations that change the ring state. Two of these displace the ring center by $l=\frac{1}{2}a$ along $\langle 100\rangle$ directions; and the other, by $l=a/\sqrt{2}$ along $\langle 110\rangle$ directions. The latter displacement is illustrated in Fig. 5, and the former in Fig. 6 [Fig. 6(b) schematizes the activated state]. Assuming stochastic JT reorientation, there are (on a time scale greater than that for the hydrogen ring motion) 18 distinct displacements that change the ring state, with a 2:1 ratio of $\langle 100\rangle$ to $\langle 110\rangle$ displacements.

Returning to the question of relative rates (JT reorientation versus hydrogen ring motion), an upper bound to the ring motion is given by coherent tunneling. Its frequency is exponentially sensitive to the potential barrier between equivalent sites and to the distance of the tunneling level below the barrier top; at sufficiently high temperatures, tunneling on excited levels can be dominant.[32] Excited hydrogen optical levels in the Vb metals are only 0.1–0.2 eV above ground,[1(a)] and are thus very much in play at normal temperatures where most diffusion measurements have been made. This gives a wide range of possibilities for the effective coherent tunneling rate, but a value of 10^{12} sec^{-1} is a

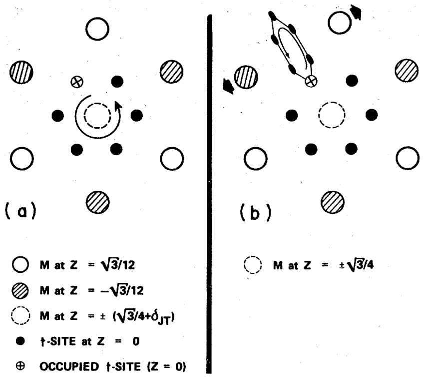

FIG. 5. Hexagonal ring of equivalent t sites normal to JT distortion axis. View is along $\langle 111\rangle$ (a) Distortion axis normal to plane of figure; (b) reorientation of distortion axis followed by hydrogen ring motion (represented by circular arrow) on a new ring. Heavy arrows indicate the new distortion axis.

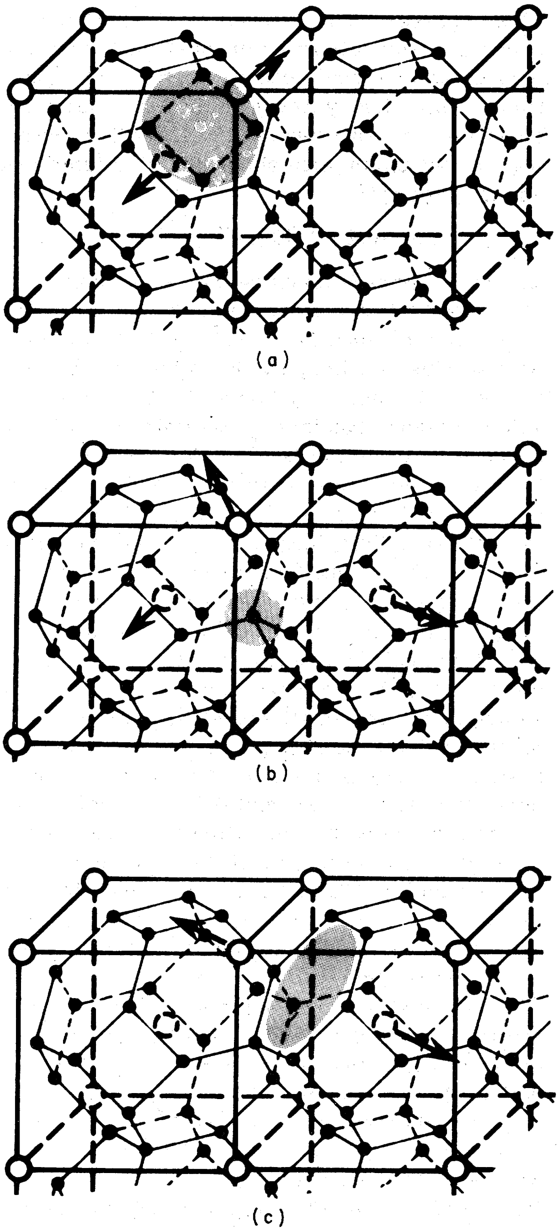

FIG. 6. Hydrogen diffusion step: (a) tunneling state before JT reorientation; (b) reorientation step with proton on indicated site; (c) tunneling state after reorientation. Arrows indicate the distortion.

probable upper limit.

To get an estimate of the JT reorientation frequency, we refer again to impurity-vacancy pairs in silicon.[29(a)] These systems have a dynamic JT process analogous to that proposed here, involving electronic reorientation among three equivalent, statically distorted defect configurations. The lifetime τ of reorientation from EPR measurements is[29(a)]

$$\tau^{-1} \simeq \exp(-0.065\ \text{eV}/kT)10^{12}\ \text{sec}^{-1}. \qquad (7)$$

This expression corresponds to either thermal excitation over a barrier or an Orbach process through an electronic excited state.[31] The mean time-of-stay for hydrogen in the Vb metals can be estimated from observed diffusivities, requiring only an assumption about diffusive jump length, and is given by[33]

$$\tau_H^{-1} \simeq \exp(-0.1\ \text{eV}/kT)10^{13}\ \text{sec}^{-1}, \qquad (8)$$

assuming *jumps between nearest-neighbor t sites*, In the present model, however, *the basic diffusive step is displacement of the JT distortion axis*. As described earlier, the jump length has only two possibilities: $l = \frac{1}{2}a$ or $a/\sqrt{2}$. The larger value is made plausible by assuming an Orbach process in which the excited electronic state is that corresponding to a static JT stabilization via the B_1 mode in Fig. 4. Actually, NMR measurements[34] on α-NbH$_x$ lead to the conclusion that $2.9 \lesssim l^2 \lesssim 7.3$ Å^2, which brackets only the larger jump length ($\langle 110 \rangle$ displacements). Using $a/\sqrt{2}$ as jump length, the nonexponential factor for τ_H^{-1} in Eq. (8) is reduced to about 2×10^{12} sec^{-1}. In either case, the important points are (i) estimated values of τ_H^{-1} are small enough at most temperatures that the assumption of rapid ring motion on hexagonal rings is plausible (at least in a coherent-tunneling regime); and (ii) the magnitude of τ_H^{-1} approximates reorientation rates observed for vacancy pairs in silicon. If the latter constitutes a reasonable yardstick for JT reorientation in the present case, then observed hydrogen diffusivities are consistent with the notion that JT reorientation is the limiting step.

While the above arguments help establish plausibility, they do not of themselves tangibly support the idea that Jahn-Teller reorientation limits diffusion. In fact, there is compelling evidence not only for this idea, but also for the idea that the reorientation involves a resonance state lying near E_F. The basis for this assertion is the existence of a dispersion step in the T_1 acoustic-phonon branch (corresponding to the elastic constant C') for the α-phase hydrides of Nb and Ta.[1(a)] High-resolution neutron-scattering measurements[35] on NbH$_{0.15}$ at 623 K reveal a relaxation process whose characteristic time agrees with the dwell time of the hydrogen atoms (as obtained from diffusion measurements). Similar effects have been observed in Nb and Ta for C, N, and O interstitials (at much lower frequencies),[35] and the dispersion steps are known here to arise from the Snoek effect, i.e., orientational relaxation of an elastic dipole. But this interpretation fails on two counts for interstitial H: (i) the strength of the Snoek effect is far too small (only an upper limit is known); and (ii) the observed amplitude of the relaxation at zero wave vector (as measured by the change in C') shows very little temperature dependence, contradicting the required T^{-1} dependence of the Snoek effect.[35]

The present model predicts a relaxation between the four distinct $\langle 111 \rangle$ directions possible for the JT distortion of Fig. 3(b). It is easily seen that this distortion couples only to the C' shear mode and gives two energetically distinct orientations. Sturge[36] has shown that the amplitude of such a relaxation, as measured by the change in the appropriate elastic constant, is

$$\Delta C \simeq -N\beta^2/kT, \qquad (9)$$

where N is the number of Jahn-Teller ions, and β is essentially the splitting of the electronic state per unit strain. Values of $\beta \simeq 3-10$ eV have been estimated for Al$_2$O$_3$:Ni^{3+} and for impurity-vacancy pairs in Si, all of which exhibit very strong Jahn-Teller coupling ($E_{JT} \simeq 0.5$ eV).[31] Taking this as a probable range for β in the Vb metal hydrides and using Eq. (9) with $N \simeq 10^{21}$ cm^{-3} per 1-at.% hydrogen and $T = 300$ K, gives a magnitude for ΔC that is at least a *hundredfold greater* than observed magnitudes.[37] Thus, Eq. (9) severely overestimates the effect; moreover, like the Snoek effect, it predicts a T^{-1} temperature dependence.

This apparent contradiction is resolved upon recognition of the fact that ψ_{JT} is not a localized electronic state but a *resonance state*. This means that it is spread out in energy and is made up of a sum of contributions from conduction-band states.[18] Relaxation via thermal redistribution among perturbed states is restricted by the Pauli exclusion principle to those band states that lie approximately within kT of the Fermi level. Thus, Eq. (9) must be modified by a factor of the order of kT/E_F, which at once removes the temperature dependence and brings the calculated magnitude of $\Delta C'$ in line with observation. A more accurate estimation of the elastic susceptibility would require a treatment paralleling Anderson's determination of magnetic susceptibility of resonance states.[18] An important difference would be the use of a negative effective U in the present case.[38] Clearly, the existence of a moderately strong relaxation effect requires in this model that the Jahn-Teller resonance state have appreciable density at E_F, agreeing with our earlier assumptions about ψ_{JT}.

The above discussion shows that the existence of an elastic relaxation process, with a temperature-independent amplitude and a characteristic frequency that correlates with hydrogen diffusion, is predicted by the present model, viz, that hydrogen diffusion is limited by Jahn-Teller reorientation of a resonance state located near the Fermi level. This reinforces the idea that hydrogen dynamics in the Vb metals consists of rapid motion (coherent tunneling) between deep-welled t sites on hexagonal rings, together with occasional diffusive hops between rings limited by Jahn-Teller reorientation. At a more basic level, it gives substance to the proposed resonance state ψ_{JT}. The description of hydrogen diffusion given in this section is not unlike Stoneham's concept,[4] but it appears here as a natural consequence of the preceding fundamental proposition.

V. EXCESS PARTIAL ENTROPY

The orientation degeneracy of ψ_{JT} has further implications; there are four distinct ways in which hydrogen can occupy a given t site, but this should show up as a ln4 contribution to hydrogen partial entropy. In fact, there is ample evidence for just such a contribution. Much effort has been devoted to measurement and analysis of excess hydrogen partial entropy, defined as the difference between observed partial entropy and the ideal solution value in the limit of small hydrogen concentrations.[8(a)] This quantity has been analyzed into contributions associated with changes in acoustic modes (S_a), electronic contributions (S_e), localized modes (S_0), and a term $k \ln\beta$ (k is the Boltzmann constant) representing configurational entropy, with $\beta = 6$ for t site occupancy. The first three terms can be reasonably well determined from measurements of phonon spectra, specific heat, and optical frequencies of hydrogen.[1(a)] There has been some confusion about the effect of acoustic modes,[8(b)] but the analysis of Magerl *et al.*[8(a)] is correct.[39] For hydrogen in Pd, where $\beta = 1$, there is no discrepancy.[40] On the other hand, for hydrogen in Nb or Ta at about 700°K, $S_a + S_e + S_0 + k \ln 6 \simeq 1.5k$,[8(a)] versus measured values of $2.5k$–$2.8k$.[8(b)] The discrepancy is removed upon inclusion of the ln4 degeneracy term predicted by the present model. Admittedly, the measurements by Pryde[9] at 400° K do not show a discrepancy. But this must be recognized as an individual determination, using an indirect method (only Kleppa's technique[8(b)] can be considered direct), of a quantity that is difficult to measure accurately, in a temperature region where difficulties are likely to be maximal.

VI. PROPERTIES AT HIGHER CONCENTRATIONS: BLOCKING RULE

Until now we have restricted the discussion to small C_H. Certain experimental facts and theoretical considerations encourage us to leave this relatively safe region of concentration space and extend the basic concepts developed thus far to the entire range of pseudo-bcc structures, viz, for $C_H \lesssim 1$. For example, many hydride properties near $C_H \simeq 1$ are noted more for their similarities to the pure metal than for their differences. Furthermore, for temperatures $\gtrsim 500°$ K, there is a continuous solid solution phase for $0 \leqslant C_H \lesssim 1$, with important properties (e.g., phonon spectra, hydrogen diffusivities, structure) showing a small, nearly regular variation over the whole range of C_H.[1] In this phase the hydrogen atoms are highly disordered relative to one another. Surprisingly, this disorder deviates appreciably from simple random occupancy of t sites, and, in fact, hydrogen on a given site blocks at least five nearest-neighbor sites with little or no effect on more distant sites.[41] This blocking effect is most visible in the form of a sharply decreasing entropy near $C_H \simeq 1$ for all the Vb hydrides, in spite of the fact that maximum occupancy of t sites gives $C_H = 6$.

On the theoretical side, the Hamiltonian with site-diagonal disorder [Eq. (6)] derived for hydrogen-atom impurities in transition metals can be considered in the case of the Vb metals as modeling a binary alloy of the form M-M', with M corresponding to the pure metal and M' representing MH_6, i.e., full occupancy of t sites. The model calculations of Velicky *et al.*[16] for binary transition-metal alloys with a Hamiltonian-like Eq. (6), using the CPA technique and a semielliptical form to approximate the d band, show that, near the top of the band, states having significant local character persist up to impurity concentrations (M'/M) of at least 0.16 (so long as the disorder parameter is not too small). While there is no straightforward correspondence of the present problem to these model calculations, we consider the similarities as sufficient to support the notion that the induced, localized d state described earlier has significance over the whole range of concentrations, $C_H \lesssim 1$. In fact a strong JT distortion, producing topological disorder, makes this notion even more plausible.

Thus we assume that the distorted state ψ_{JT} is an especially stable entity and that properties of the Vb bcc hydrides are dominated throughout by its molecular character. Stated differently, the idea of a negative effective U, giving a strongly localized, spin-paired resonance state,[38] together with the Pauli exclusion principle, suggests a closed-shell molecule. In particular, we can formulate a "blocking rule" based on the assumed integrity of ψ_{JT}. In the absence of any evidence to the contrary, it is certainly conceivable that more complicated induced electronic states based on dimeric, etc., impurity configurations might become important with increasing hydrogen concentration. But we have already described the apparent existence of blocking effects contradicting this notion; furthermore, Huang-diffuse-scattering measurements[42] on α-TaH$_x$ give no indication of cluster effects up to the highest impurity concentrations studied ($C_H \simeq 0.2$). Armed with these facts, we can construct various configurations involving two hydrogen atoms on neighboring t sites, circumscribed by the corresponding induced d states. With the aid of intuitive ideas about molecular systems, we can then develop blocking rules by disallowing configurations that appear to disrupt the integrity of ψ_{JT}. Figure 7 shows some examples of neighboring impurity polyhedra in which the induced d states are represented by delineating the four ⟨111⟩ bonds associated with each t site.

Careful consideration of structures like those in Fig. 7 suggests the following blocking rule: *configurations in which adjacent polyhedra share a* ⟨111⟩ *edge are forbidden.* Thus in Fig. 7, only configuration a is forbidden. Configuration b has two shared M atoms, but the two t_{2g} orbitals on each of these atoms can be arranged to give mutually orthogonal induced states for the two polyhedra. The same is true of c which has one shared atom; while for configuration d one of the t_{2g} orbitals on the shared atom must be used for both induced states. We assume that the latter situation is not a disruptive perturbation for the isolated resonance state. For configurations like those of Fig. 7 the relative location of distortion axes is considered to be determined by static lattice (elastic) interactions,[43] which are assumed to be much smaller than the repulsive electronic interaction implied by the blocking rule. This rule is based on the qualitative conclusion that, so long as neighboring polyhedra do not share a ⟨111⟩ edge, the induced state for each polyhedra is of the form ψ_{JT} and is (at least approximately) orthogonal to the neighboring resonance states.

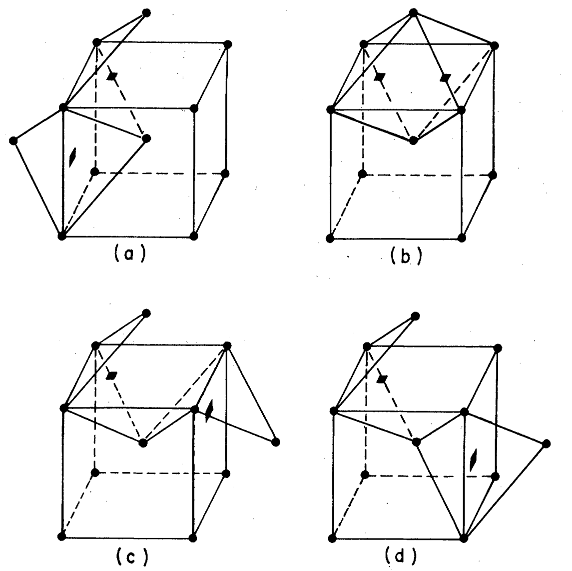

FIG. 7. Dimeric configurations of impurity polyhedra. Small squares (distorted) represent hydrogen atoms on t sites. Diagonal lines represent quasimolecular bonds.

The blocking rule formulated above is especially easy to apply because of the fact that every t site lies at the intersection of four hexagonal rings. Every site on these four rings shares at least one ⟨111⟩ edge with the site in question. Conversely, if a t site shares one or more ⟨111⟩ edges with the site in question, then the two sites belong to one or more common hexagonal rings. Figure 8 illustrates the blocking effect, showing a total of seventeen blocked sites, including the occupied site. While blocking is thermodynamically unimportant at sufficiently small concentrations (thus earlier conclusions concerning excess hydrogen partial entropy are not affected), it not only has significant thermodynamic consequences at higher C_H (hydrogen partial entropy sharply reduced from ideal), but also has an important dynamical effect: *hydrogen diffusion will be highly correlated*. This latter prediction has been experimentally verified by proton-NMR measurements of H diffusion in α-NbH$_x$$D_y$.[44] For a given value of $x+y$, diffusion parameters measured for

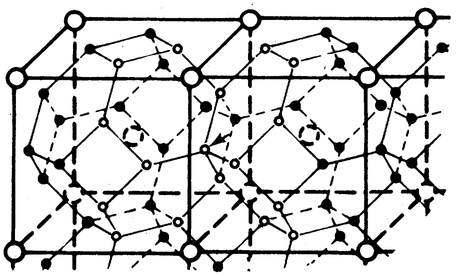

FIG. 8. Illustration of blocking rule (see text). All hollowed t sites are blocked when site indicated by arrow is occupied.

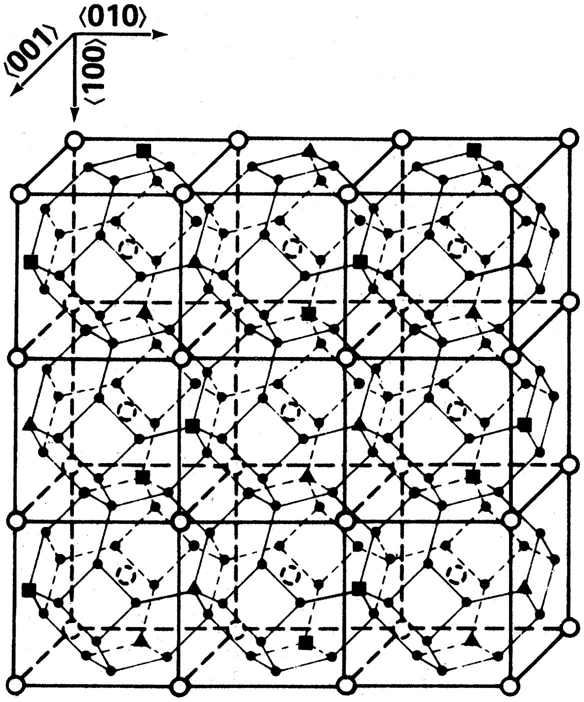

FIG. 9. β-Ta_2H superstructure. Squares represent occupied sites and triangles represent those unoccupied sites that are not blocked.

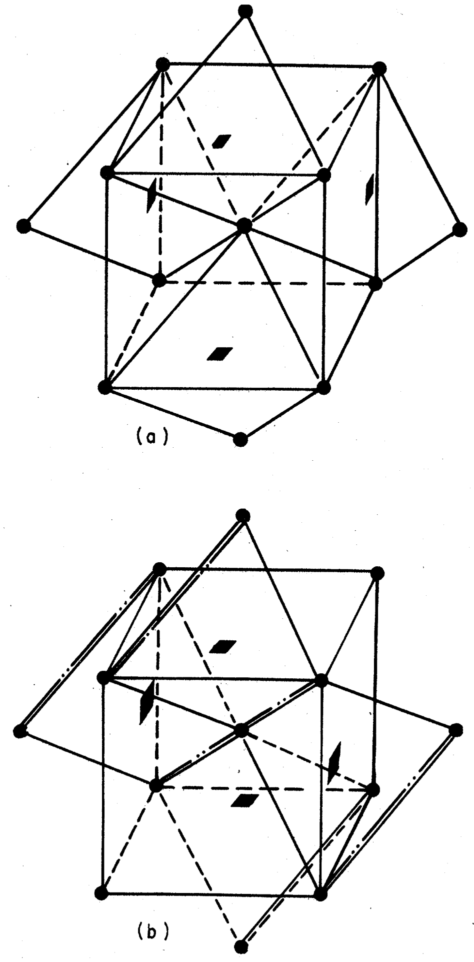

FIG. 10. Arrangement of impurity polyhedra in (a) γ-NbH and (b) β-NbH (double lines represent shared ⟨111⟩ edges).

H with decreasing x, approach values measured for D at the same total concentrations.

Figure 9 shows the Ta_2H β-phase structure[1(b)] in which hydrogen occupies all the z_1 sites (there are six sublattices of t sites, with two subsets each of x, y, and z types) in alternate (110) planes of z sites. Using the blocking rule with the help of its graphic representation in Fig. 8, it can easily be shown that for the β-Ta_2H structure of Fig. 9, (i) the blocking rule is not violated and (ii) all empty sites except the z_1 sites in empty (110) planes of z sites are blocked. Clearly, the z_1 sites can be filled giving the fully ordered high-concentration, low-temperature γ-NbH structure[1(b)] illustrated in Fig. 10(a). Given that there are only four ⟨111⟩ edges per M atom, *this is the maximum stoichiometry allowed* by the simple blocking rule.

VII. EXCEPTIONS TO THE BLOCKING RULE

Actually, many of the proposed superstructures for the various ordered hydride phases violate the simple blocking rule. An example of this is β-NbH [Fig. 10(b)]: a relatively high-temperature superlattice phase exhibiting a fairly broad range of compositions in which hydrogen atoms occupy allowed t sites randomly.[1(b)] Figure 10(b) reveals that occupied polyhedra each share two noncontiguous ⟨111⟩ bonds having one shared bond with each of two adjacent occupied polyhedra. This clearly contradicts the proposed ψ_{JT}, which has a distortion along only one of the four ⟨111⟩ bonds. On the other hand, it is consistent with a state derived from a static JT distortion corresponding to the B_1 mode shown in Fig. 4. The two shared ⟨111⟩ axes for a given polyhedron in Fig. 10(b) are most likely bonding (and compressed) and the other two nodal (and enlongated). The t_{2g} orbitals for the bonding axes must be independent of those for the antibonding axes, as the former holds twice as many screening electrons as the latter; but this presents no difficulty. Apparently, an electronic state stabilized by the B_1 distortion is in play, lending credibility to the earlier idea that the activation step for hydrogen diffusion involves an Orbach process through this state.

Beyond these violations of the simple blocking rule, there is an additional feature needing con-

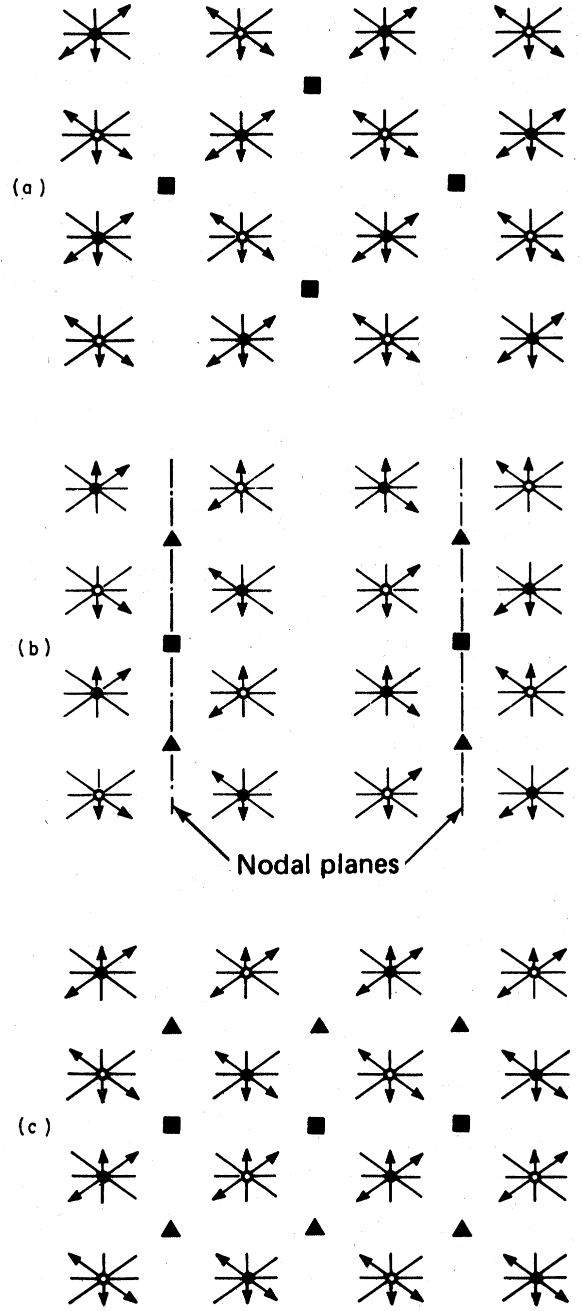

FIG. 11. (a) β-Ta$_2$H or β-NbH structure viewed along [110]; (b) β-Ta$_2$H viewed along [$\bar{1}$10]; (c) β-NbH viewed along [$\bar{1}$10]. Coordinates are given by Fig. 9. Closed and open circles are M atoms at $z=\frac{1}{4}\sqrt{2}$ and $-\frac{1}{4}\sqrt{2}$, respectively. Squares and triangles are H atoms at $z=0$ and $\pm\frac{1}{2}\sqrt{2}$, respectively. For definition of bars and arrows see text.

sideration. Metal sublattice structural parameters observed[45] for β-Ta$_2$H near 300° K are inconsistent with any reasonable arrangement of single distortion axes expected for ψ_{JT}. However, it is not difficult to show, at least qualitatively, that the structure is consistent with an ordered assemblage of B_1-distorted electronic states. This is illustrated in Figs. 11(a) and 11(b) where the β-Ta$_2$H structure is seen, respectively, along ⟨110⟩ and ⟨$\bar{1}$10⟩ directions (coordinates are shown in Fig. 9). The t_{2g} d lobes are represented by sets of lines on each metal atom directed along the eight nearest-neighbor ⟨111⟩ directions. The significance of the arrows is as follows: →← represents a bonding interaction (lobes in phase); → – represents a nodal situation or an antibonding interaction (lobes have opposite phase); while – – represents metallic phasing corresponding to absence of localized electronic effects on ⟨111⟩ edges that do not belong to impurity polyhedra. Figure 11(b) shows nodal planes between alternate (110) planes of metal atoms while Fig. 11(a) shows enhanced bonding between ($\bar{1}$10) planes of metal atoms. This is in accord with structural details observed for β-Ta$_2$H[1(b)] showing an alternating displacement of metal atoms along ⟨110⟩ with the lattice parameter along ⟨110⟩ greater than that along ⟨$\bar{1}$10⟩.

The β-NbH structure shown in Figs. 11(a) and 11(c) can be related to the β-Ta$_2$H structure in a very simple way. Hydrogen atoms go to those z sites [in the empty (110) planes of t sites, Fig. 11(b)] that share ⟨111⟩ bonding edges with contiguous impurity polyhedra. In this structure the two independent t_{2g} orbitals per M atom with lobes oriented (approximately) along nearest-neighbor ⟨111⟩ directions, lie, respectively, in ($\bar{1}$10) and (110) planes. Figure 11(c) shows nodal planes between all pairs of (110) planes of metal atoms for β-NbH consistent with observed concentration dependence of superstructure parameters for β-NbH$_x$.[46] Note that in this scheme the NbH stoichiometry can be exceeded by adding hydrogen atoms to empty (110) sites of Fig. 11(a). But these additional polyhedra have shared ⟨111⟩ edges that are nodal; furthermore, the necessary occupancy of second-nearest t sites [Fig. 7(b)] is likely to be somewhat repulsive. Even so, β-NbH shows a tendency to go slightly beyond $C_H=1$ before transforming to fcc NbH$_2$.[1(b)]

The exceptions described in this section appear to invalidate the simple blocking rule, but it should be noted that the γ-NbH phase [Fig. 10(a)]—which has also been observed for TaH—is a pseudocubic, low-temperature, high-concentration phase.[1(b)] The cubic metal sublattice is consistent with an assemblage of noncontiguous polyhedra based on ψ_{JT} and having parallel distortion axes. Also supporting the simple blocking rule are deuteron-magnetic-resonance studies[47] showing that in superlattice phases, D atoms jump only between z-type sites, and thus x- and y-type sites, rather than being merely metastable, are apparently blocked.

In any case, the various superlattice electronic structures based on either of the two JT resonance states and depicted in Figs. 10 and 11 are clearly not like molecular (Van de Walle) solids, but seem more closely akin to an extended molecular network with delocalized valence bonds (e.g., aromatic hydrocarbons) or perhaps to a strongly hydrogen-bonded network (e.g., H_2O).

We conclude this section with a brief discussion of a different kind of exception: the fact that in V, for larger values of C_H, octahedral sites (o sites) play an important role. In fact, β_1-V_2H and β-V_2D are almost exclusively based on o-site occupancy.[48,1(b)] In this regard, we simply note that from the observed linear variation of elastic constants with C_H in VH_x,[37] one can estimate their values at $C_H = 0.5$ by simple extrapolation. Especially interesting is the observation that the quantity $(C_{11} - C_{12})/2C_{44}$ decreases from a value of 1.3 at $C_H = 0$ to extrapolated values of 0.24 for V_2D and 0.08 for V_2H. This suggests that the shift to o-site occupancy in V is associated with lattice instability.[49]

VIII. SUMMARY AND CONCLUSION

In this paper we have demonstrated the possibility for transition metals of a hydrogen-induced d-band resonance state localized primarily on the shell of metal atoms nearest to interstitial hydrogen. The theoretical basis for this state is the existence for the d band of an Anderson Hamiltonian having essentially site-diagonal disorder brought on by orthogonalization of the hydrogen 1s state with pseudo-plane-wave states.

Under the assumption that spatial characteristics of the induced state are determined by the appropriate tight-binding atomic orbitals, a set of symmetrized MO's was constructed for the four-atom, D_{2d} quasimolecule circumscribing an occupied t site in bcc Vb metals. Locations of the MO's relative to the Fermi level were qualitatively determined by relating their bonding character to that of the bcc d band. It was shown that a doubly degenerate nonbonding state, $\psi_t(E)$, met the requirements of availability (describable as a summation over unoccupied d states) and closeness to the Fermi level, and was thus a reasonable candidate for accommodation of screening electrons. But existence of spatial degeneracy admits the possibility of stabilizing Jahn-Teller distortions. By comparing $\psi_t(E)$ with states associated with reasonably well-understood systems, it was shown that a large Jahn-Teller effect (~1 eV) could reasonably be expected for $\psi_t(E)$.

This feature turned out to be pivotal, providing a possible key for understanding certain anomalies (hydrogen diffusion, hydrogen partial entropy, cubic-lattice distortion) and at the same time justifying the highly qualitative approach leading up to $\psi_t(E)$. Most notably, it was shown that a particular distortion, involving displacement along a single $\langle 111 \rangle$ bond, suggests a remarkable mechanism for diffusion based on the interplay between reorientation of the JT distortion axis and rapid motion of hydrogen about this axis on hexagonal rings. This diffusion model was shown to predict relaxation effects observed for one of the acoustic phonon branches. In particular, it explained the absence of a T^{-1} temperature dependence as a manifestation of the Pauli exclusion principle acting on a resonance state.

Another highlight was the demonstration that over the whole range of interesting compositions, the Vb bcc metal hydrides could plausibly be construed as an assemblage of localized states and that properties at higher concentrations are determined primarily by the persistence of these states in either of two stabilized configurations. In particular, it was shown that highly correlated diffusion, blocking effects, maximum concentration, and superlattice structures (including small distortions of the metal sublattice) could all be understood on this basis.

If the description presented in this paper is essentially correct, then the hydrogen-induced quasimolecular d state must be considered as a novel instance of electron localization[50] in solids. Moreover, the present study suggests a new approach for treating not only other transition-metal hydrides, but perhaps the whole problem area of light interstitials in transition metals—at least in the dilute limit. Admittedly, the occurrence of qualitative features playing such a dominant role, as for the Vb hydrides, is probably exceptional. Furthermore, persistence of local character with increasing C_H in the Vb hydrides may well be primarily a result of topological disorder introduced by the stabilizing distortion. Even so, it is worth considering whether or not an LCAO-MO theory of resonance states induced by light interstitials in transition metals has a more general validity.

How can the model set forth in this paper be effectively tested? Probably the most fruitful testing ground will be quasielastic neutron-scattering (QNS) measurements which, in principle, give highly detailed information about hydrogen dynamics within the host metal.[6] Analysis will not be straightforward, however. First of all, conventional assumptions about hydrogen diffusion in metals, which worked so well for analysis of QNS measurements on PdH_x,[5] are here inappropriate. The dynamics in the present instance are compounded of a highly nonstochastic hydrogen tunneling on hexagonal rings (the ring sites are probably occupied stochastically) and a more or less stochastic JT reorientation process (the implied caveat is simply that JT hops may be restricted to $\langle 110 \rangle$ displacements as discussed in Sec. IV). Besides these complications, there are the blocking effects which, because of the extent of the blocked region (see Fig. 8), are likely to be important even at the lowest practical concentrations. Nevertheless the problem should be reasonably tractable. Apart from the dynamics of diffusion, QNS (through the Debye-Waller factor) also gives the vibrational amplitude of the proton.[1(g)] According to the present model for diffusion, that amplitude is likely to be appreciably greater in the direction of hydrogen motion on hexagonal rings than in other directions, especially if coherent tunneling is involved. This should appear as a particular anisotropy in a larger-than-normal Debye-Waller factor, giving a potentially important test for the diffusion model.

A second promising area is the low-temperature work on NbH_xO_y, implicating hydrogen tunneling modes on a small ring of t sites.[7] If it can be demonstrated that hydrogen atoms are locally independent of interstitial oxygen atoms and that tunneling takes place on hexagonal rings, then the present model will gain direct support. Experiments using the positive muon as a probe,[1(h)] can also address this question.

Another interesting study already under way is the experimental comparison of hydrogen in solid solution NbTa alloys with hydrogen in the pure metals. Actually, results from measurements of solvus concentration (the concentration of hydrogen at which a new hydride phase first precipitates) at various temperatures and various alloy compositions[51] provided the initial impetus for the ideas presented in this article. Under the conventional description of hydrogen in metals (in which electrons generally play a minor, if not uninteresting role), this seems a dull experiment simply because Nb and Ta, as well as their hydrides, are so much alike. In fact, the study (which was conceived as a base-line determination) revealed a striking nonlinearity in the solvus concentration as a function of alloy composition,[51] with a pronounced maximum at about $Nb_{0.3}Ta_{0.7}$. Even more dramatic results are observed for NbV alloys.[52] Since local symmetry is crucial in the present model, the existence of highly nonlinear behavior upon disrupting that symmetry by alloy formation is no longer a surprising result—it is to be expected. Here, too, quantitative analysis will be difficult because the solvus represents the coexistence of two phases, and both must be included in the analysis. Also, there is the liklihood of pseudo-Jahn-Teller effects,[53] in which nearby states have a Jahn-Teller interaction comparable to their energy separation, so that a stabilizing distortion is possible even in the absence of strict degeneracy. In spite of these difficulties, further study of NbTa and NbV alloy hydrides should help determine the veracity of the proposed quasimolecular resonance state.

The pervasive impact of this surprisingly simple electronic resonance state on the behavior of the bcc Vb hydrides is remarkable, encompassing such diverse and seemingly unrelated properties as lattice distortion, hydrogen diffusion, elastic relaxation, hydrogen partial entropy, blocking effects, and superlattice structures. Indeed the behavior of hydrogen in the Vb metals, as described here, represents a dramatic demonstration of the importance of Anderson's pioneering ideas[50] about electron localization in disordered crystalline environments.

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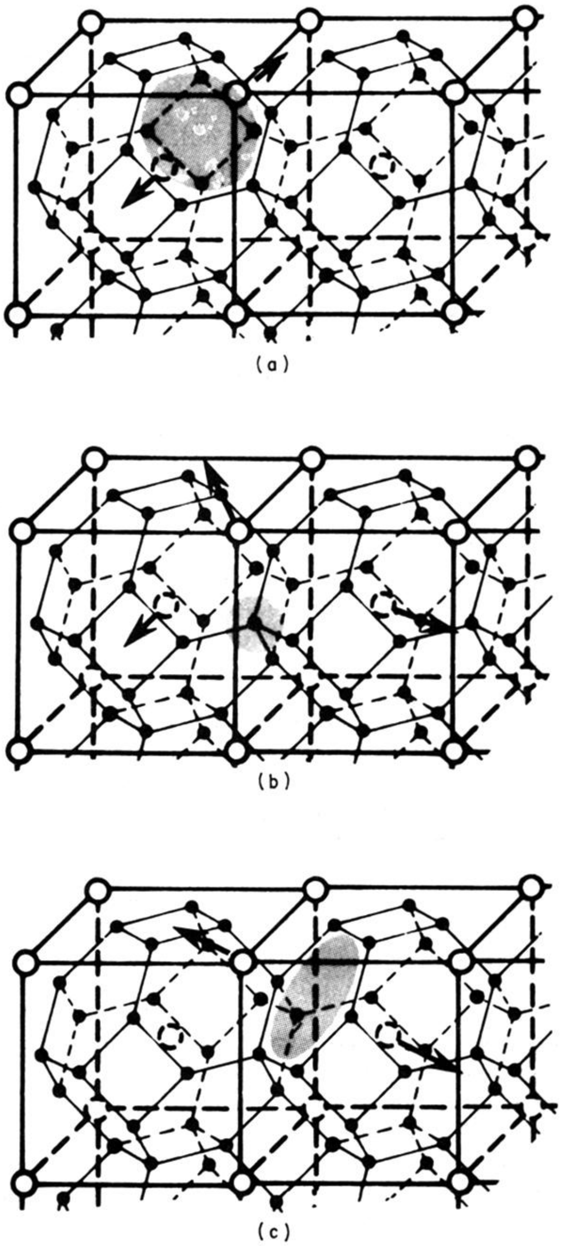

FIG. 6. Hydrogen diffusion step: (a) tunneling state before JT reorientation; (b) reorientation step with proton on indicated site; (c) tunneling state after reorientation. Arrows indicate the distortion.