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Jahn-Teller A_nB_{4-n} resonance polaron model for amorphous metals

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Jahn-Teller polaron resonances localized on A_nB_{4-n} clusters provide a microscopic basis for two-level tunneling centers and for nonmagnetic Kondo anomalies in amorphous metals. The most active tunneling centers belong to a mixed-valence regime, while in a different regime, the model gives a pseudospin Kondo Hamiltonian with a cutoff $\sim\omega_D$. The virtual-state model is used to obtain analytic expressions for the adiabatic polaron potentials.

I. INTRODUCTION

The low-temperature properties of amorphous solids are universally consistent with a distribution of intrinsic two-level tunneling centers of unknown origin.[1(a)] Many amorphous *metals* are further characterized by a resistivity varying as $-\ln T$ over some temperature range $0<T\lesssim\Theta_D$.[1–3] This logarithmic anomaly is apparently of a nonmagnetic origin[3–5] (it exists even in amorphous ferromagnets[1(b)] well below T_C) in spite of the fact that such behavior has been established only for isolated magnetic impurities (i.e., the Kondo problem[6]). It is known that the "noncommutative" model for scattering of conduction electrons by two-level centers gives a nonmagnetic Kondo effect.[7] The essential feature of this model is the assumption of a conduction-electron assisted tunneling process which is additional to the coupling due to scattering amplitude variation with tunneling-center configuration. But in the absence of a microscopic model for the tunneling centers, these couplings can only be guessed at and a key physical feature of the problem may well be overlooked.

The concept of Jahn-Teller (JT) polaron resonances was recently introduced[8] to explain the behavior of hydrogen in the group-V*b* metals (V,Nb,Ta). Subsequent studies[9] revealed the indirect role of hydrogen and suggested that JT polaron resonances might be an intrinsic feature of transition metals. A model Hamiltonian representing a single JT center coupled to conduction-band states was seen to be analogous to the Anderson Hamiltonian for magnetic impurities in metals.[10] An important difference is that the JT model is characterized not by a localized magnetic moment, but by a localized symmetry-lowering distortion corresponding to a small polaron with an internal degree of freedom. Such a center might thus give rise to a nonmagnetic Kondo effect. The model also gives a multiple-well potential for the polaron resonance and therefore provides a possible microscopic basis for the existence of tunneling centers in amorphous metals.

This paper presents various adiabatic potential functions for the JT polaron based on the intermediate-coupling virtual-state model.[10] These potentials reveal an interesting range of possibilities in relation to the properties of amorphous metals. We also present arguments showing that the JT Hamiltonian is usually equivalent to a nonmagnetic pseudospin Kondo Hamiltonian with a cutoff for spin-flip scattering given approximately by the Debye energy $k_B\Theta_D$.

II. THE JT HAMILTONIAN

We start with the following Hamiltonian:

$$H_{\rm JT}=\sum_{k,\sigma}\epsilon_k n_{k\sigma}+\epsilon_d\sum_{\sigma}n_{d\sigma}+\lambda(n_{d+}-n_{d-})Q+(P^2+\mu^2\omega^2Q^2)/2\mu+\sum_{k,\sigma,s}(V_{kd}c^\dagger_{k\sigma s}c_{d\sigma s}+\text{H.c.})\;, \tag{1}$$

with

$$n_{j\sigma}=\sum_s c^\dagger_{j\sigma s}c_{j\sigma s}\;,$$

where $j=k$ or d, $s=\uparrow$ or $\downarrow$ is the electron spin, and $\sigma=+$ or $-$ labels the orbital partners of the degenerate $\Gamma(E)$ representation. The different terms in H correspond, respectively, to (i) the $\Gamma(E)$-band kinetic energy, (ii) a degenerate set of localized orbitals orthogonal to the band states, (iii) the JT coupling of the degenerate orbitals to a local shear coordinate Q, (iv) an Einstein-oscillator representation of the local coordinate with reduced mass μ and frequency $\omega\approx(\omega_D\equiv k_B\Theta_D/\hbar)$ and (v) a hopping interaction between local and band states which we call $H_{\rm mix}$. We assume Coulombic interactions are fully screened. The localized orbitals were originally pictured[8] as a combination of atomic *d* orbitals belonging to the degenerate $\Gamma(E)$ representation of a tetragonal M_4H cluster embedded in a *bcc* lattice of metal atoms M. It was proposed that the hydrogen potential (which is directly coupled only to metal states belonging to the fully symmetric representation) modifies the local parameters of (1), resulting in the stabilization of a JT polaron resonance localized on the M_4H cluster. In this article, we associate the localized orbitals with any nominally tetragonal A_nB_{4-n} cluster in a disordered metallic system. The index σ of Eq. (1) labels the nominally degenerate pair of cluster orbitals according to whether they are symmetric or antisymmetric with respect to one of the C_2' operations of the tetragonal

(D_{2d}) point group. We assume that the band states in a disordered system may be meaningfully classified in the same way, such that states strongly scattered by one of the degenerate polaron configurations are, in lowest order, orthogonal to those scattered by the other polaron configuration. This orthogonality may be understood in terms of the nodal patterns associated with the projection of the relevant band states onto a local combination of tight-binding orbitals adjacent to and interacting with the $\Gamma(E)$ cluster orbitals.

To simplify the discussion and to provide analytic results, we use the virtual-state model[10] for the projection of the total density of $\Gamma(E)$ states onto a spin state of the local orbital $|d\sigma\rangle$, i.e.,

$$\pi\rho_{d\sigma}(\epsilon,E_\sigma)=\Delta/[(\epsilon-E_\sigma)^2+\Delta^2] , \qquad (2)$$

where $\Delta=\pi\langle V^2\rangle_{\text{av}}\rho$ and ρ is the density of the $\Gamma(E)$ band states (assumed constant). The strength of the lattice coupling is given by the parameter $C\equiv\lambda^2/\mu\omega^2$; when $C\gg\Delta$, the uncoupled conduction band plus impurity provides a meaningful zeroth-order description.

Figure 1 is a configurational representation of the isolated four-atom cluster or "molecule" showing schematically the adiabatic, noncrossing energy surfaces for the various molecular states based on the $\Gamma(E)$ orbitals. The potentials are labeled by the corresponding total occupancy $n\equiv n_{d+}+n_{d-}$ and pseudospin $S\equiv|n_{d+}-n_{d-}|/2$. The $n=1,3$ potential implies a Coulomb repulsion for these charge states, but we expect that Coulombic effects will be largely screened out in the intermediate-coupling regime. Beneath the minima at $S_z=0$, ±1 [$S_z\equiv(n_{d+}-n_{d-})/2$] are shown the molecular structures corresponding to $Q_e=0,\mp2C/\lambda$. The lowest few oscillator levels in the $S_z=-1$ well are also depicted. The solid and dashed arrows represent two quite distinct kinds of transitions that are possible for this molecular system The solid arrow corresponds to a Franck-Condon (vertical) process for which the excitation frequency is much larger than ω; the transition takes place in such a short interval that structural relaxation is not possible. Vertical transitions cannot provide intermediate states for the pseudospin-flip process ($S_z=\pm1\rightarrow S_z=\mp1$). The dashed arrows, on the other hand, correspond to processes for which the excitation frequency is much smaller than ω; the structure relaxes adiabatically to the corresponding minimum. These slow processes *do* provide intermediate states for the pseudospin flip, and thus are of special interest in this study. The Born-Oppenheimer or adiabatic approximation ignores these latter processes which, although contributing insignificantly to the total interaction, may in certain cases profoundly alter the ground state (e.g., as in the theory of superconductivity[11]).

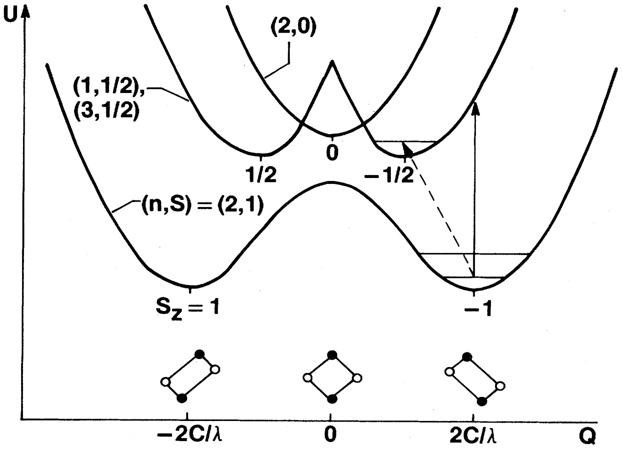

FIG. 1. Schematic potential surfaces for the different electronic configurations based on the $\Gamma(E)$ orbitals of an isolated M_4 cluster ($n\equiv n_{d+}+n_{d-}$, $2S\equiv|n_{d+}-n_{d-}|$, and $2S_z\equiv n_{d+}-n_{d-}$). Cluster geometries at the $S_z=0$, ±1 minima are viewed along the unique twofold axis. Open and closed circles represent M atoms above and below the figure plane.

III. ADIABATIC POLARON POTENTIALS

Before considering the ground-state implications of the nonvertical processes, we discuss H_{JT} in the adiabatic approximation, which treats Q as a parameter. Green's-function methods[10] now give the result (2), with a self-energy term that depends explicitly on Q, i.e., $E_\sigma=\epsilon_d+\sigma\lambda Q$. To analyze the Q dependence of the total energy, we apply the Hellman-Feynman theorem to H_{JT} with the result[12]

$$\frac{\partial U_1}{\partial Q}=2\lambda\int_{-\infty}^{\epsilon_F}[\rho_{d+}(\epsilon,\epsilon_d+\lambda Q)-\rho_{d-}(\epsilon,\epsilon_d-\lambda Q)]d\epsilon+\mu\omega^2 Q . \qquad (3)$$

Thus, extrema of the potential surface U_1 satisfy

$$C\langle n_{d+}-n_{d-}\rangle=-\lambda Q_{e1} , \qquad (4)$$

where $\langle n_{d\sigma}\rangle=2\int^{\epsilon_F}\rho_{d\sigma}d\epsilon$ is the mean occupancy of the local orbital $|d\sigma\rangle$, which is implicitly a function of Q. Equation (4) is always satisfied at $Q=0$; it may also have solutions at $Q=\pm Q_{e1}$ corresponding to formation of a polaron resonance in a double-well potential. The symmetric limit of the virtual-state model (i.e., $\epsilon_d=\epsilon_F$) has $\langle n_{d+}+n_{d-}\rangle=2$ for any Q, and the condition for polaron formation is $4C/\pi\Delta\geq1$. This paper is concerned primarily with the intermediate-coupling regime, i.e., $C\simeq\Delta$ for which polaron formation is a borderline proposition. We suppose that an amorphous metal may be considered as an array of distinct four-atom clusters which, because of chemical disorder, are characterized by a reasonably smooth distribution for the local parameters ϵ_d and C. We assume that H_{JT} has the same kind of significance here as does the single local-moment model for the theory of local magnetic moments in transition metals.[13] If the parameter distribution is not too sharp, the concentration of polaron-resonance centers should be relatively small. For the sake of concreteness, we take the rectangular distributions $|\epsilon_d-\epsilon_F|\leq2\Delta$ and $\Delta/2\leq C\leq2\Delta$. In this region of parameter space, the virtual-state model reveals an interesting diversity. To see this, first note that the mean occupancy is explicitly[10]

$$\pi\langle n_{d\sigma}\rangle=2\cot^{-1}[(\epsilon_d-\epsilon_F+\sigma\lambda Q)/\Delta] . \qquad (5)$$

Substituting Eq. (5) into Eq. (3) and integrating the resulting expression with respect to Q gives

$$\pi U_1(q)/C = \pi q^2/2 + p\{\ln[p^2+(x-q)^2] + \ln[p^2+(x+q)^2] - 2\ln(p^2+x^2)\}$$
$$-2\{(x-q)\tan^{-1}[(x-q)/p] + (x+q)\tan^{-1}[(x+q)/p] - 2x\tan^{-1}(x/p)\}\ , \qquad (6)$$

with $q=\lambda Q/C$, $p=\Delta/C$, $x=(\epsilon_d-\epsilon_F)/C$, and $U_1(0)\equiv 0$. The distributions for the reduced local parameters are $|x|\leq 2p$ and $\frac{1}{2}\leq p\leq 2$. In the limit $p\rightarrow 0$, Eq. (6) goes over to an Anderson "negative-U" model[14] (without the Hubbard electronic repulsion) symmetric about $q=0$. In this limit the double-well polaron ($q_e=\pm 2$) is stable relative to the (metastable) $q=0$ configuration for $|x|\leq 1$, while it is metastable in the range $1\leq |x|\leq 2$ and unstable when $|x|>2$. For the intermediate-coupling regime ($p\sim 1$), these boundaries are diminished and the region of metastability is sharply compressed.

The energy scale is also appreciably reduced. This is illustrated in Fig. 2, which shows U_1 vs q for several values of x in the range 0.6–0.9. Comparison of curve *d* ($p=0.5$, $x=0.6$) with the dashed curve ($p=0.7$, $x=0.6$) shows the sharp reduction of the energy scale with increasing p. When $p=0.7$, the region of metastability is practically nonexistent. The potential barriers in the triple-well potentials (b) and (c) of Fig. 2 are on the order of $0.05C$. This is sufficient to localize the A_nB_{4-n} oscillator in one of the wells, under the reasonable assumption that C is on the order of 1 eV and ω is on the order of 0.01 eV. Using Eq. (5), it can be shown that for the potentials (b) and (c) the total occupancy ($\langle n_{d+}+n_{d-}\rangle$) changes by about one electron in going from the well at $q=0$ to one of the wells at $\pm|q_e|$. The region of metastability is therefore a valence-fluctuation regime. In the presence of static random strain, a certain fraction of those centers characterized by triple-well potentials should exhibit tunneling between the $q=0$ configuration and one of the off-center configurations, due to a coincidence of the corresponding minima. A broad, relatively uniform distribution of tunneling and energy-level parameters should follow as a consequence of the very strong dependence of U_1 on p and x, as illustrated in Fig. 2.

This model thus seems able to reproduce the essential features of the phenomenological Anderson-Halperin-Varma-Phillips (AHVP) two-level tunneling model,[15] which has been so successful in decreasing the low-temperature properties of amorphous materials. The JT polaron model provides as well a basis for metastability and slow relaxation effects, which are also characteristic features of the amorphous state.

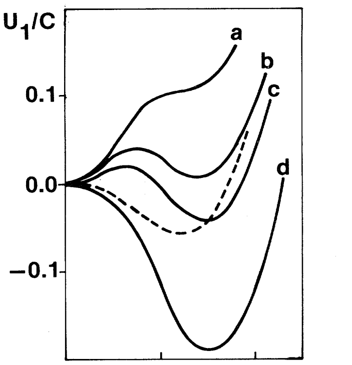

FIG. 2. Adiabatic virtual-state-model JT polaron potentials, illustrating region of metastability for intermediate coupling. Solid curves have $p=0.5$ and (a) $x=0.9$, (b) $x=0.8$, (c) $x=0.75$, (d) $x=0.6$. Dashed curve has $p=0.7$ and $x=0.6$ $[U(-Q)=U(Q)]$.

IV. KONDO REGIME

What about those four-atom centers for which the double-well polaron resonance is strongly stabilized, as in curve *d* of Fig. 2? We will attempt to show that for intermediate coupling, this is a Kondo regime. To simplify the discussion, we consider only the particle-hole symmetric case ($\epsilon_d=\epsilon_F$).

It can be anticipated from the orthogonality catastrophe theorem[16] that at sufficiently low temperatures the above description breaks down. In fact, the adiabatic approximation is not a good starting point for a correct description of the true ground state of H_{JT}. To show why this approach ultimately fails, we go back to the original Hamiltonian (1) and apply the Schrieffer-Wolff (SW) transformation,[17] treating H_{mix} (the last term in H_{JT}) as a perturbation. Referring back to Fig. 1, we now want to determine the role of the slow or nonvertical processes that were previously ignored. The perturbation (H_{mix}) couples the distinct manifolds associated with $S_z=0,\pm\frac{1}{2},\pm 1$; but now in doing perturbation theory, it is important to distinguish between virtual excited states corresponding on the one hand to fast (vertical) processes and on the other to slow processes. As in the theory of superconductivity,[11] we assume that excitations with $|\epsilon_k-\epsilon_{k'}|<\omega$ are slow processes during which the molecule relaxes adiabatically to its corresponding excited-state minimum (inverse adiabatic approximation). If $C\gg\Delta$, the rest of the interaction will not substantially alter the energy surfaces of Fig. 1. In this limit two distinct slow steps are required for the spin flip: one for $S_z=\pm 1\rightarrow S_z=0$, and the other for $S_z=0\rightarrow S_z=\mp 1$. The effective operator corresponding to the pseudospin-flip process is thus a two-body term rather than the one-body term of the Kondo Hamiltonian. Thus, the regime $C\gg\Delta$ gives an effective two-body interaction between $|k+\rangle$ and $|k-\rangle$ particles, but it does not give an effective Kondo Hamiltonian.

How do we attack the problem in the intermediate-coupling regime, i.e., when $C\simeq\Delta$? The above procedure ignores the major part of the interaction and focuses entirely on pseudospin-flip scattering processes. But when $C\simeq\Delta$, the isolated-molecule energy surfaces of Fig. 1 may no longer be relevant to a discussion of these slow processes. To determine the appropriate adiabatic surfaces for pseudospin-flip scattering, we assume that the adiabatic solution described by Eqs. (3) and (4) is usually adequate. We suppose that the polaron resonance is in its pseudospin-down configuration ($S_z<0$) for which the average occupancy of the $|d+\rangle$ state is small but nonzero. We now imagine a slow scattering event in which an electron hops from a state $|ks+\rangle$ near the Fermi level into one of the $|d+\rangle$ levels at $\epsilon_{d+}=\epsilon_d+\lambda Q$ with $Q>0$. That level is then temporarily unavailable for conduction-band mixing, but the remaining impurity channels are open. The resulting slow occupancy drives the molecule impurity toward a new configuration (as for the $S_z=-1$ to $S_z=-\frac{1}{2}$ transition of Fig. 1), but now we allow the remaining electrons to adjust adiabatically to any change in Q through their coupling with the available impurity channels. The Hellman-Feynman theorem now gives for $Q>0$

$$\frac{\partial U_2}{\partial Q}=\lambda+\lambda\int_{-\infty}^{\epsilon_F}[\rho_+(\epsilon,\epsilon_d+\lambda Q)-2\rho_-(\epsilon,\epsilon_d-\lambda Q)]d\epsilon+\mu\omega^2 Q\ . \quad (7)$$

The first term is the energy to transfer an electron from the Fermi level to the local state $|ds+\rangle$ for unit value of Q. The integral term now involves only the three impurity levels available for mixing during the slow process. Equation (7) is not valid for $Q=0$ because the degeneracy of $|d+\rangle$ and $|d-\rangle$ in that case precludes assigning the "slow" electron exclusively to $|ds+\rangle$.

The extremal condition for the adiabatic energy surface U_2 of the excited impurity is (for $Q>0$)

$$\lambda Q_{e2}=C(\langle n_{d-}-n_{d+}/2\rangle-1)\ . \quad (8)$$

For $p\equiv\Delta/C$ sufficiently small, Eq. (8) goes over to the isolated-molecule result $Q_{e2}=C/\lambda$, corresponding to the $S=\frac{1}{2}$ potential of Fig. 1. As p increases to some critical value p_c, the minima of the $S=\frac{1}{2}$ double-well potential gradually disappear. Thus, in the range $4/\pi>p>p_c$, the system relaxes during a slow process to the high-lying minimum at $Q=0$ of an $S=0$ potential before returning to one of the ground-state minima. (For $p>4/\pi$, the ground-state minimum is at $Q=0$.) In the virtual-state model, the right-hand side of Eq. (8) is analytic and a graphical solution gives $p_c\simeq 0.3$ for the symmetric case.

Thus, in the intermediate-coupling regime ($p\simeq 1$), a significant region of the relevant parameter space ($1.27>p>0.3$) has only the one high-lying minimum at $Q=0$. As an example, Fig. 3 shows the fully (U_1) and partially (U_2) adiabatic-potential surfaces for the virtual-state model with $x=0$ and $p=0.7$. The analytic expression for U_2 with $x=0$ is (for $q>0$)

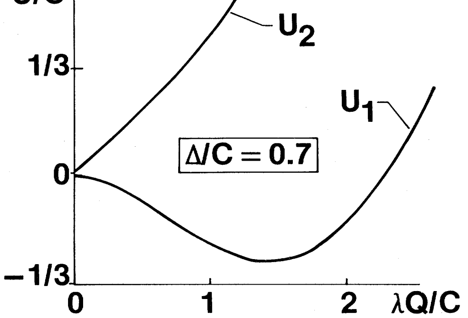

FIG. 3. Potential surfaces U_1 and U_2 corresponding to the full and partial adiabatic approximation, respectively [Eqs. (6) and (9)], with $x=0$, $p=0.7$, and $U_2(0)\equiv 0$.

$$\frac{2\pi U_2(q)}{C}=\frac{2\pi U_2(0)}{C}+\pi q(1+q)+3p\ln(1+q^2/p^2)-6q\tan^{-1}(q/p)\ , \quad (9)$$

where $U_1(0)$ is the zero of energy. At $q=0$, the only difference between U_1 and U_2 is that for U_2 one of the local states does not mix with the band states, and thus[18]

$$U_2(0)=\int_{-\infty}^{\epsilon_F}(\epsilon_F-\epsilon)\rho_{d\sigma}(\epsilon,\epsilon_d)d\epsilon\ . \quad (10)$$

This integral diverges using Eq. (2), but a realistic model should give $U_2(0)\simeq\Delta=pC$ when $\epsilon_d=\epsilon_F$. This must be added to the energy difference $[U_2(0)-U_1(q_e)\simeq 0.3C]$ between the minima in Fig. 3 [which for convenience has $U_2(0)=0$] to obtain the total energy difference between ground- and excited-state minima. For the example shown, this gives $E_2-E_1\simeq C$, which is the characteristic magnitude for the range $4/\pi>p>p_c$. In this range only a single slow-scattering event (e.g., electron hops from $|ks+\rangle$ to $|ds+\rangle$, then from $|ds'-\rangle$ to $|k's'-\rangle$ with $|\epsilon_k-\epsilon_{k'}|<\omega$), with a virtual excitation energy C, is required for the pseudospin-flip process. Because of particle-hole symmetry when $x=0$, we assume the same virtual excitation energy applies when the above scattering sequence is interchanged. If the problem for the symmetric case is now formally represented by the symmetric Anderson model with $U=2C$, the SW transformation gives[17] an effective nonmagnetic Kondo Hamiltonian in which the spin operators represent pseudospin rather than electron spin, i.e.,

$$H_{\text{ex}}=\sum_{ks}\sum_{k's'}J_{kk'}(\Psi^{\dagger}_{k's'}\hat{S}\Psi_{ks})(\Psi^{\dagger}_{ds}\hat{S}\Psi_{ds'})\ , \quad (11)$$

where $\Psi^{\dagger}_{js}\equiv(c^{\dagger}_{j\sigma s},c^{\dagger}_{j\bar{\sigma}s})$ with $j=k$ or d, $s=\uparrow$ or $\downarrow$, $\bar{\sigma}=-\sigma$, and $2\hat{S}$ are the Pauli matrices. The coupling constant is

$$J_{kk'}\equiv-(4V_{kd}V^{*}_{k'd}/C)\Theta(|\epsilon_k-\epsilon_{k'}|-\omega)\ . \quad (12)$$

A crucial feature is the cutoff at ω as given by the step function Θ [$\Theta(x)=1$ if $x\le 0$ and $\Theta(x)=0$ if $x>0$]. While the formal representation as a symmetric Anderson model is not strictly correct, the antiferromagnetic nature of the interaction between the local and conduction-band pseudospin follows from the same considerations[19] that give $J<0$ for the Hartree-Fock solution of the Anderson model. Namely, the doubly occupied impurity pseudospin state below ϵ_F is repulsive while the one above ϵ_F is attractive because it can be occupied by (either spin-up or spin-down) band electrons having the same pseudospin (σ) as the empty impurity orbital. Given that the exchange Hamiltonian (11) applies only to the intermediate-coupling regime, it follows that $\rho|J|\simeq\Delta/C$ is on the order of unity. While this might appear to invalidate an SW perturbation expansion,[17] it should be noted that the SW result for the symmetric Anderson model is relevant even when $\rho|J|$ is not small.[20]

An important feature of the JT Kondo Hamiltonian is that spin-up and spin-down electrons belonging to one of the orbitally degenerate $\Gamma(E)$ band states have the same antiferromagnetic interaction with the impurity pseudospin. At temperatures well below $T_k \sim \omega \exp(1/\rho J)$ there should be[19] a spin-pairing condensation of $\Gamma(E)$ band electrons in the vicinity of the impurity, exactly compensating the impurity pseudospin. The electron condensation should in turn drive a relaxation of lattice phonons opposing that of the local phonon Q; this effect, however, is beyond the scope of this study. The primary goal of this section is to demonstrate that the single impurity JT polaron model gives, for an appreciable range of the relevant parameter space, an effective nonmagnetic Kondo Hamiltonian. The cutoff for this latter Hamiltonian is similar to that used in the theory of superconductivity. It represents an upper bound for electronic excitations that allow relaxation (i.e., "tunneling") of the local phonon Q from one pseudospin configuration to the other. The important consequence of this cutoff is that the Kondo temperature for the JT model scales down from ω, which is on the order of the Debye frequency.

V. CONCLUSION

The significance of this model is that it provides a microscopic basis for nonmagnetic Kondo phenomena in the range $T < \Theta_D$, and also for other properties of amorphous metals as embodied in the AHVP model.[15] Careful analysis of particular transition-metal systems must go beyond the virtual-state model used in this study, but the crucial feature in the local density of states is undoubtedly the existence of a relatively narrow peak containing an appreciable fraction of the spectral density.

A more complete treatment would also include explicitly the repulsive Coulombic interactions between electrons in the local orbitals. Besides the kind of local minima described here, such a model also gives a magnetic JT polaron resonance.[9(c)] The idea that four-atom JT polaron resonances play a considerable role in determining transition-metal properties must be considered as somewhat speculative. In fact there is no direct and compelling evidence for their existence in any particular system. Perhaps the most promising systems for the purpose of establishing the existence of these centers are the dilute hydrides of the V*b* metals, where the model[8] gives a polaron resonance at every hydrogen site. We have already proposed[9(b)] that a resistivity study of such a system might show a hydrogen-related nonmagnetic Kondo effect. A recent low-temperature study[21] of crystalline $\mathrm{NbTi}_{0.05}(\mathrm{H,D})_x$ revealed a hydrogen-induced, isotope-independent, glasslike specific heat anomaly. This is consistent with the original concept[8] of hydrogen-stabilized JT polaron resonances, if the distribution of local hydrogen environments is not too narrow.

We conclude this article with a brief justification for the special emphasis in this model on four-atom clusters. It is well known in LCAO theories of small molecules that certain orbital topologies are extremely unfavorable[22] and usually exist only as high-energy intermediates between alternative stable covalent-bonding configurations. Foremost among these are symmetrical four-electron, four-orbital topologies. The overwhelming ascendancy in nature of the shared-pair covalent bond is, to a large extent, the nearly universal avoidance of this unfavorable interaction topology. Close-packed metals are an exception to this rule; here the local instability of symmetrical four-atom topologies relative to the covalent-bond topology is offset by the kinetic energy stabilization of band formation. Under certain circumstances, the balance between these opposing tendencies will be a delicate one; the four-atom instability may manifest itself in unusual ways. We assert that this model addresses the latter situation.

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