Ab Initio Calculation of Crystalline Electric Fields and Kondo Temperatures in Ce Compounds

J. E. Han,[1,2] M. Alouani,[1,3] and D. L. Cox[1,2]
[1]Department of Physics, The Ohio State University, Columbus, Ohio 43210
[2]Institute for Theoretical Physics, University of California, Santa Barbara, California 93106-4030
[3]IPCMS, Université Louis Pasteur, 23 rue de loess, Strasbourg, France

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We have calculated the band-f hybridizations for Ce$_x$La$_{1-x}M_3$ compounds ($x = 1$ and $x \to 0$; $M =$ Pb, In, Sn, Pd) within the local density approximation and fed this into a noncrossing approximation for the Anderson impurity model applied to both dilute and concentrated limits. Our calculations produce crystalline electric field splittings and Kondo temperatures with trends in good agreement with experiment and demonstrate the need for detailed electronic structure information on hybridization to describe the diverse behaviors of these Ce compounds. [S0031-9007(96)02231-4]

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A pressing theoretical issue for strongly interacting electronic materials is to produce realistic descriptions including crystalline environment and symmetry effects, well treated by *ab initio* electronic structure theory, together with dynamical effects best treated by many body formalisms. A case in point is heavy fermion materials with strongly interacting f-electron states that give rise to huge electronic mass enhancements. Some understanding of these systems has been reached in Anderson model approaches which assume a nearly atomic limit picture for f states that hybridize with extended conduction states through matrix elements determined from electronic structure (local density approximation or LDA) calculations [1–5]. In particular, Gunnarsson and Schönhammer [1] and Monnier *et al.* [6] have calculated high energy spectra for a number of cerium based metals with a $T = 0$ variational method, which however ignored crystal field effects. The LDA has been used to estimate hybridization-induced crystalline electric field (CEF) splittings in cerium systems [3] without including the strong correlations. Second order perturbation theory in the direct Coulomb interaction gives good estimates for electron mass enhancements while only partially capturing Kondo effect physics [5].

In this work, we present first results for a method which combines a nonperturbative, finite temperature diagrammatic approach for the Anderson model (the noncrossing approximation or NCA) with input parameters from the LDA. The NCA can properly generate hybridization induced CEF splittings while giving an excellent description of the Kondo effect. We report calculations of the CEF splittings and Kondo scales T_K in CeM_3 ($M =$ Pb, In, Sn, Pd) compounds in which experimental T_K values vary with M by nearly 3 orders of magnitude. We have computed energy dependent hybridization matrix elements within the LDA in two limits.

(1) For the dilute alloy system Ce$_x$La$_{1-x}M_3$ with $x \to 0$.
(2) For concentrated CeM_3 compounds.

We correctly find a stable Γ_7 doublet CEF ground state with small T_K values for CePb$_3$ and CeIn$_3$ and large T_K values with negligible CEF effects for CeSn$_3$ and CePd$_3$.

In our work, the CEF splittings are induced by band-f hybridization, which is anticipated to be the dominant contribution [4]. This splitting arises as follows: a CEF state in Ce-f^1 configuration is shifted downward by level repulsion through virtual $f^1 \to f^0 \to f^1$ and $f^1 \to f^2 \to f^1$ charge fluctuations. In the presence of crystalline anisotropy, different irreducible representations (irreps) of the point group in the f^1 manifold receive different shifts. Using this idea in second order perturbation theory, Wills and Cooper [3] estimated the contribution of the hybridization-induced CEF splittings on top of extrapolated point charge contributions [7]. Although the electrostatic potential from the cubic environment can induce the CEF (i.e., in the point charge model), it is difficult to produce a good estimate of this contribution in a metal due to conduction electron charge screening [7] and metallic covalency. We shall neglect point charge contributions in this Letter.

We describe the Ce$_x$La$_{1-x}M_3$ systems in terms of effective impurity Anderson models [8,9] in the dilute ($x \to 0$) and concentrated ($x = 1$) limits at a site of cubic symmetry relevant to the Cu$_3$Au structure. In this Letter, we ignore intersite interaction effects such as the antiferromagnetism found in CeIn$_3$ [10] and CePb$_3$ [8]. The impurity Anderson Hamiltonian of interest reads

$$\begin{aligned} H = & \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \\ & + \frac{1}{\sqrt{N_s}} \sum_{\mathbf{k}\sigma,m} (V_{\mathbf{k}\sigma m} c_{\mathbf{k}\sigma} f^\dagger_m + H.\text{c.}) \\ & + \sum_m \epsilon_{fm} f^\dagger_m f_m + U \sum_{m<m'} n_{fm} n_{fm'}, \end{aligned} \tag{1}$$

where m is the label of cubic irrep states, $V_{\mathbf{k}\sigma m}$ the hopping matrix element between conduction electron

($c_{\mathbf{k}\sigma}$) and f orbital (f_m), N_s the number of sites, ϵ_{fm} the f-level energy measured from the Fermi level, U the on-site Coulomb repulsion for f electrons.

We have used $\epsilon_{fm} = -2.0$ eV for Hund's ground multiplet ($J = \frac{5}{2}$) in all the calculations, consistent with experimental [11] and theoretical [12] values. The spin-orbit (SO) splitting $\Delta_{\rm SO}$ was read off from the separation between $J = \frac{5}{2}$ and $J = \frac{7}{2}$ peaks in the Ce $4f$ projected density of states (DOS). We find $\Delta_{\rm SO} = 0.35$ eV for all M, in agreement with atomic values. We set the on-site Coulomb repulsion $U \to \infty$ in our many body approximation, though we partially correct for this as we shall describe below. In the cubic point group symmetry of the CeM_3 compounds, the $J = \frac{5}{2}$ multiplet decomposes into a Γ_7 magnetic doublet ($|\frac{5}{2};\Gamma_7\rangle$) and Γ_8 quartet ($|\frac{5}{2};\Gamma_8\rangle$), split by an energy Δ_{78}. The $J = \frac{7}{2}$ multiplet splits into Γ_6 and Γ_7 doublets, and a Γ_8 quartet. Experimentally, the Γ_7 doublet lies lowest for $M = \mathrm{Pb}, \mathrm{In}$ ($\Delta_{78} > 0$), while no CEF splitting is resolved for $M = \mathrm{Sn}, \mathrm{Pd}$.

The hybridization strengths are calculated from the LDA using the linearized muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) including the combined correction term [13]. We assumed the same Wigner-Seitz radii for Ce and M ($= \mathrm{Pb}, \mathrm{In}, \mathrm{Sn}$) and used experimental lattice constants. We used 165 **k** points in the irreducible Brillouin zone with DOS integrations carried out by the tetrahedron method [14].

In the concentrated limit ($x \to 1$, i.e., CeM_3), we define the hybridization $\Gamma^{\rm med}_{mm'}(\epsilon)$, in terms of an effective *impurity* Anderson model, with the hybridization derived from the overlap between f orbital at the origin and the rest of the lattice. More specifically

$$\Gamma^{\rm med}_{mm'}(\epsilon) = -\mathrm{Im} \sum_{\mathbf{R},\mathbf{R}'} V_{\mathbf{R}m} V^*_{\mathbf{R}'m'} G'(\mathbf{R}, \mathbf{R}', \epsilon + i\eta) , \qquad (2)$$

where $V_{\mathbf{R}m}$ is the hopping matrix element between mth f orbital and ligand orbital at $\mathbf{R}$ and $G'(\mathbf{R}, \mathbf{R}', \epsilon + i\eta)$ the Green's function of ligand electron created at $\mathbf{R}$ and recovered at $\mathbf{R}'$, with the central f orbital excluded. Now the array of ligand and f orbitals (origin excluded) serves as an effective *static* medium coupled to the f orbital at the origin. Our method follows Gunnarsson *et al.*'s suggestion [15] to interpret the f-projected DOS as the spectral function of an effective *noninteracting* resonant level model. This corresponds to the first iteration of a "dynamical mean field theory" to the interacting problem [16], which becomes exact in infinite spatial dimensions. We obtain the hybridization as follows:

$$\Gamma^{\rm med}_{mm'}(\epsilon) = -\frac{i}{2}[\mathbf{G}^{\rm LDA}(\epsilon + i\eta)^{-1} - \mathbf{G}^{\rm LDA}(\epsilon - i\eta)^{-1}]_{mm'}$$

$$G^{\rm LDA}_{mm'}(\epsilon \pm i\eta) = \int dz \frac{\rho^{\rm LDA}_{mm'}(z)}{\epsilon \pm i\eta - z} , \qquad (3)$$

where $G^{\rm LDA}_{mm'}(\epsilon \pm i\eta)$ is the matrix Green's function, $\rho^{\rm LDA}_{mm'}(\epsilon)$ the f-projected DOS derived from the LDA.

In the impurity limit ($x \to 0$), we calculate the hybridization between f and *bare* ligands, that is,

$$\Gamma^{\rm imp}_{mm'}(\epsilon) = \pi \sum_{\mathbf{k}\sigma} V^*_{\mathbf{k}\sigma m} V_{\mathbf{k}\sigma m'} \delta(\epsilon - \epsilon_{\mathbf{k}\sigma}) , \qquad (4)$$

which corresponds to Eq. (2) of Ref. [6]. While, in the concentrated limit, the f electron hops into bonding states of the f (origin excluded) ligand lattice, this impurity limit hybridization accounts for the overlap of f and ligand states. We apply it to the impurity limit of Ce$_x$La$_{1-x}M_3$ since the Ce-Ce hopping is negligibly small for $x \to 0$. The procedure for computing $V_{\mathbf{k}\sigma m}$ is to set up a Hamiltonian matrix of a *lattice* resonant level model for CeM_3. We construct a Hamiltonian matrix in an orthogonal basis using eigenvectors and eigenvalues of LMTO equation in the *one-center* expression [13]. After diagonalizing the ligand sector of the matrix and unitary transforming the f-ligand sector with the new ligand basis, we directly read off hybridization matrix elements, $V_{\mathbf{k}\sigma m}$. The Brillouin zone sum of Eq. (4) is performed with the tetrahedron method [14]. We used lattice constants of LaM_3 compounds and readjusted the Fermi energy such that the ligand bands are filled up with $N_e - 1$ electrons, with N_e the number of valence electrons per CeM_3 unit cell. The minus one accounts for the removal of the single Ce $4f^1$ electron in the $x \to 0$ limit.

As seen in Fig. 1, despite the different procedures used to calculate them, the hybridizations of the $x \to 0$ and

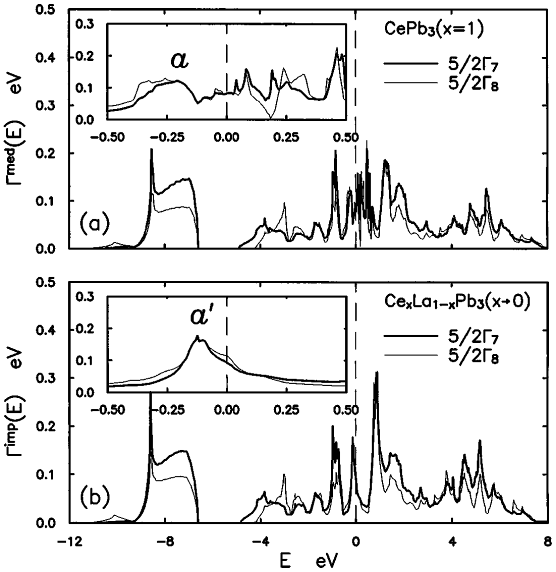

FIG. 1. Hybridizations of Ce$_x$La$_{1-x}M_3$ in two different limits. (a) $x = 1$ limit. Larger hybridization for Γ_7 doublet (thick line) near 1.0–3.0 eV pushes $|\frac{5}{2};\Gamma_7\rangle$ below the Γ_8 quartet (thin line). (b) $x \to 0$ limit. Curves are almost identical to (a) except near the Fermi energy. Note that the peak a' is pushed down to peak a [inset (a)] due to f-ligand coupling.

$x \to 1$ limits are almost identical in the high energy region ($|\epsilon - E_F| \geq 0.5$ eV). In the low energy region (insets of Fig. 1), the peak a in the impurity limit is pushed down to peak a' due to the presence of Ce f orbitals in the effective medium. Since the Kondo temperatures (T_K) depend upon the hybridization weight below the Fermi energy (E_F), this bonding effect near E_F can lead to a completely different scale of T_K as x changes. The extra structure in the $x \to 1$ calculation above E_F (dashed line) is due to flat f bands. Although this feature above E_F is qualitatively different from the $x \to 0$ limit, it contributes little to Δ_{78}.

We solved the $U \to \infty$ Anderson model by using the well known noncrossing approximation which gives a good quantitative description of Ce compounds except for $T \leq T_p \ll T_K$ (where T_p is a "pathology scale" signaling breakdown of the approximation) [2]. To the first order expansion in $1/N_g$, with N_g the ground multiplet degeneracy, the spectral functions of the f^0 and f^1 states are solved for from coupled self-consistent nonlinear integral equations for the f^0, f^1 self-energies. To partially correct for our $U \to \infty$ approximation, we have estimated the contribution to Δ_{78} arising from virtual f^2 occupancy between $|\frac{5}{2};\Gamma_7\rangle$ and $|\frac{5}{2};\Gamma_8\rangle$ by employing second order perturbation theory with $U = 6$ eV. We then added the resulting shifts to the *bare* f-level positions in the NCA. Δ_{78} values were read off from separation of the peaks of $|\frac{5}{2};\Gamma_7\rangle$ and $|\frac{5}{2};\Gamma_8\rangle$-$f^1$ spectral functions, which include contributions to all orders in V^2, as per Levy and Zhang [4] and in contrast to Wills and Cooper [3]. The Kondo temperatures T_K were computed by fitting the magnetic susceptibility curves to NCA calculations for Lorentzian DOS where the analytic expression of T_K is well known [2].

The CeM_3 compounds (M = Pb, In, Sn) have the doublet ($|\frac{5}{2};\Gamma_7\rangle$) states as the lowest lying multiplet with Δ_{78} values in good agreement with the experiments [8–10], as listed in Table I. For the heavy fermion systems CeIn$_3$ and CePb$_3$, $\Delta_{78} > 0$ (Γ_7 is stable) and $\Delta_{78} \gg T_K$, both in agreement with experiment. The CEF splitting comes from the larger Γ_7 hybridization in the energy region from 1.0 to 3.0 eV, which results in the doublet (Γ_7) ground state for M = In, Pb. Naively, since $\Delta_{78} \sim V^2$, one would expect the larger crystal field splitting for CeIn$_3$ to correspond to a much larger T_K value than for CePb$_3$ which is not seen experimentally. This common reasoning assumes, however, energy independent hybridization, clearly not the case here as shown in Fig. 2. In detail, the hybridization strength averaged over energy of CeIn$_3$ exceeds that of CePb$_3$ which dictates $\Delta_{78}|_{\mathrm{In}} > \Delta_{78}|_{\mathrm{Pb}}$, while the smaller CeIn$_3$ hybridization right below E_F (marked by an arrow in Fig. 2) yields a smaller T_K value. Apparently, detailed hybridization calculations are critical for *quantitative* understanding of real heavy fermion materials.

TABLE I. Electonic configuration of ligand atom M (EC), ground multiplet Γ_{grd}, CEF splittings Δ_{78}, and Kondo temperatures T_K for Ce$_x$La$_{1-x}M_3$ systems. Positive Δ_{78} indicates a stable Γ_7 ground doublet on the Ce sites. Units in Kelvin.

M	$\Delta_{78}^{\exp}/T_K^{\exp}$	$\Delta_{78}^{x=1}/T_K^{x=1}$	$\Delta_{78}^{x\to0}/T_K^{x\to0}$
Pb	67/3	50/0.053	45/8.8
In	183/(<11)	125/0.016	80/3.1
Sn[a]	−/450	159/400	176/238
Pd[a]	−/700	−215/3210	−314/2600

[a] [Δ_{78} not experimentally deducible for $\Delta_{78} \ll T_K$].

Despite the correct prediction of the ground CEF in CePb$_3$, there is a large discrepancy between T_K for impurity and concentrated limits. Because of the exponential sensitivity of T_K to model parameters in heavy fermion systems [17], the reliable estimation of T_K is beyond the accuracy of our approximations. Improvement in the accuracy can be made by (i) calculating the f-level energy ϵ_f as a function of x and (ii) including the La f orbital in conduction states in the impurity limit calculation [18].

The *intermediate valence* materials, CeSn$_3$ and CePd$_3$, have $\Delta_{78} \ll T_K$ due to their large hybridization, as shown in Table I. This agrees with experiment which fails to resolve CEF peaks. For CePd$_3$, the LDA yields an anomalously huge hybridization (up to 1.5 eV) between Pd d orbitals and Ce f orbitals below the Fermi energy unlike other compounds which are dominated by f-s, p overlap. As a result, the estimated T_K for CePd$_3$ was much larger than the experimental value [19]. Note that despite the common belief that T_K depends on the value

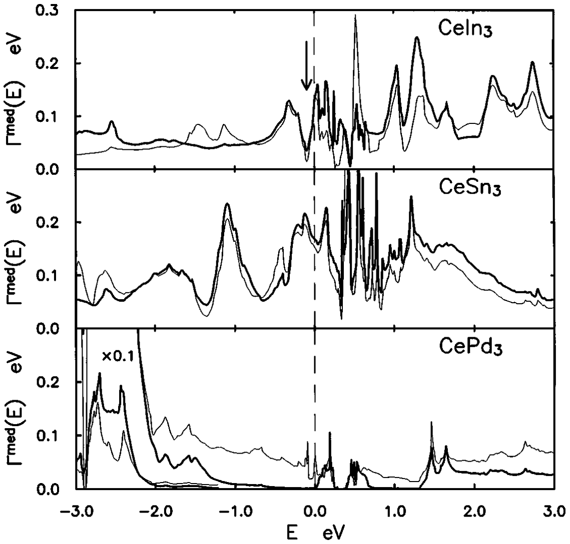

FIG. 2. Hybridizations of CeM_3(M = In, Sn, Pd). CeSn$_3$ and CePd$_3$ are in mixed valence regime due to large $\Gamma(\epsilon)$ compared to those of CePb$_3$ and CeIn$_3$. Small hybridization of CeIn$_3$ near the Fermi energy (marked by an arrow) is responsible for small T_K Note the huge contribution of Pd d orbital (scaled down by factor of 10) in CePd$_3$ to a large T_K despite the small $\Gamma(\epsilon)$ near Fermi surface. As in Fig. 1, the thick (thin) line denotes the hybridization for Γ_7 doublet (Γ_8 quartet).

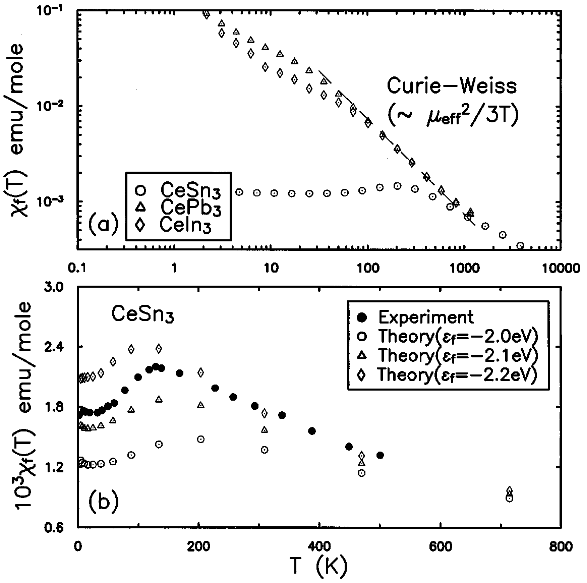

FIG. 3. Calculated magnetic susceptibility $\chi(T)$ vs T for CeM_3 compounds. (a) M dependence of $\chi(T)$; see text for discussion. (b) Magnetic susceptibilities of CeSn$_3$ for different f-level positions, ϵ_f.

of hybridization at the Fermi energy, CePd$_3$ shows a counterexample where T_K can be dominated by a large hybridization below the Fermi surface.

The magnetic susceptibility $\chi(T)$ provides a measure of the degree of screening of the local moments by conduction electrons, as shown in Fig. 3(a). For CeIn$_3$ and CePb$_3$, $\chi(T)$ deviated from Curie-Weiss behavior near $T \sim \Delta_{78}$ without sizable moment screening until the lowest accessible temperature; $\chi(T)$ of CeIn$_3$ crossed over from $|\frac{5}{2};\Gamma_7 + \Gamma_8\rangle$ to $|\frac{5}{2};\Gamma_7\rangle$ magnetic moment regime regaining inverse-T behavior at temperatures (~10–100 K) well below the CEF splitting. As opposed to Lawrence *et al.* [10], this crossover behavior of $\chi(T)$ results from partial screening of the effective magnetic moment arising from CEF splitting rather than Kondo effect.

In Fig. 3(b), susceptibility curves of CeSn$_3$ are plotted with a comparison to experiment [9]. Since $\chi(0) \sim 1/T_K$ and T_K is exponentially sensitive to ϵ_f as $T_K \propto \exp[\pi\epsilon_f/N_g\Gamma(0)]$, we performed calculations for several ϵ_f's (-2.0, -2.1, -2.2 eV). Clearly our calculations bracket but do not fit the experimental data. The calculation underestimates the bump at 130 K, which becomes prominent with orbital degeneracy due to particle-hole asymmetry. Since a calculation for $\Delta_{78} = 0$ fits the data well [20], we suspect the source of the disagreement may be an overestimate of CEF splitting in our calculation, placing the effective degeneracy between two ($T_K \ll \Delta_{78}$) and six ($\Delta_{78} = 0$).

In conclusion, we reproduced both the band and many body features of the Ce compounds by input of LDA(LMTO-ASA) calculated hybridizations into $U \rightarrow \infty$ NCA calculations for appropriately defined impurity Anderson models. We reproduce well experimental trends in T_K, Δ_{78}, and $\chi(T)$ for the CeM_3 series. This work provides a starting point for quantitative calculations of realistic heavy fermion systems at finite temperatures. Improvement may come through a proper inclusion of f^2 dynamics ($U \neq \infty$), a reliable theory for electrostatic CEF contributions, and through self-consistent closure of the many body calculations.

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[1] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983).
[2] N.E. Bickers, *et al.*, Phys. Rev. B **36**, 2036 (1987).
[3] J.M. Wills and B.R. Cooper, Phys. Rev. B **36**, 3809 (1987).
[4] P.M. Levy and S. Zhang, Phys. Rev. Lett. **62**, 78 (1989).
[5] M. Steiner, *et al.*, Phys. Rev. Lett. **72**, 2923 (1994).
[6] R. Monnier, *et al.*, Phys. Rev. Lett. **56**, 2744 (1986).
[7] R.J. Birgeneau, *et al.*, Phys. Rev. B **8**, 5345 (1973).
[8] C.L. Lin *et al.*, Phys. Rev. Lett. **58**, 1232 (1987), and references therein.
[9] D.E. MacLaughlin, J. Magn. Magn. Mater. **47&48**, 121 (1985), and references therein.
[10] J.M. Lawrence and S.M. Shapiro, Phys. Rev. B **22**, 4379 (1980).
[11] J.W. Allen *et al.*, Phys. Rev. Lett. **46**, 1100 (1981).
[12] J.F. Herbst and J.W. Wilkins, Handb. Phys. Chem. Rare Earths **10**, 321 (1987); we chose the −2.0 eV value based upon the interconfiguration energy difference curves at the Wigner-Seitz cell radius of elemental Ce.
[13] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[14] O. Jepsen and O.K. Andersen, Solid State Commun. **9**, 1763 (1971).
[15] O. Gunnarsson *et al.*, Phys. Rev. B **39**, 1708 (1989).
[16] A. Georges, *et al.*, Rev. Mod. Phys. **68**, 13 (1996).
[17] A 15% increase in the hybridization strength results in 2 orders of magnitude larger T_K for CePb$_3$.
[18] The inclusion of La f orbitals will push the peak a' toward peak a'. This effect can be calculated by a supercell calculation.
[19] The overestimated $\Gamma(\epsilon)$ values for CePd$_3$ may arise from the LDA underestimation of the $d(Pd)$-band width.
[20] E. Kim and D.L. Cox, Phys. Rev. Lett. **75**, 2015 (1995).