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Author(s): A. R. Bishop
Z. G. Yu

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MESOSCALE CHARGE-ORDERING IN TRANSITION METAL OXIDES: FORMATION AND SIGNATURES

A. R. Bishop and Z. G. Yu

Theoretical Division and Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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Abstract

We briefly outline the value of an inhomogeneous (unrestricted) Hartree-Fock plus Random Phase approach for understanding the types and properties of mesoscopic patterns of localized small polaron s in transition metal oxides. Using a multiband Peierls-Hubbard model for a hole-doped CuO_2 layer as an illustrative example, we demonstrate the appearance of correlated high-energy (electronic) and low-energy (localized phonon and spin-wave) signatures of various vertical, diagonal, metal-centered, and oxygen-centered mesoscopic stripe patterns of localized holes (small polarons).

I. INTRODUCTION

Charge localization in transition metal oxides (TMOs) has been discussed for several decades from a solid state chemistry perspective, and has an almost equally long history in terms of small polarons from a solid state physics perspective. The intense focus of the last decade on TMOs inspired by high-temperature superconducting cuprates, and more recently colossal magnetoresistance manganites, has resulted in fundamental advances in synthesis control, experimental probes in spatial and temporal domains, and theoretical techniques and insights. This period has clearly established[1] that "complex electronic materials" such as TMOs are characterized by *intrinsic* structure on multiple "mesoscopic" scales (and related multiple time scales). This mesoscale activity lies largely outside the scope of traditional solid state probes and modeling techniques designed to measure average, homogeneous, high-symmetry characteristics. The electronically/optically/magnetically active structures at mesoscales arise from strong sensitivities to small unit cell perturbations which can even appear in local density band structures or Fermi surface measurements (e.g. as flat pieces of Fermi surface), but have their full expression in new appreciations of strong *couplings* between *spin*, *charge*, and *lattice* degrees-of-freedoms.

In this newly developing appreciation for the functional role of multiscale science in electronic materials, the role of *small polarons* in TMOs has become a particularly clear example, as exemplified in these Proceedings. The "polarons" here are composites of spin, charge, and lattice and are found as essential elements of all TMOs, including high-temperature superconductors, colossal magnetoresistance manganites, and ferroelectrics, as well as many related classes of materials – probably including laves phase compounds, spinels, V_2O_3, heavy-fermion compounds, hexaborides, many organic electronic materials, etc, etc. The new experimental and theoretical techniques available open up a quite new era of probing and controlling small polarons and the materials functionalities they determine – we are positioned[2] to probe properties directly on relevant length and time scales, rather than having to rely exclusively on macroscopic measurements (transport, thermodynamics and so

on).

Having accepted the prevalent presence and role of small polarons, attention must focus on: (a) Developing fully nonadiabatic descriptions of polarons and polaron responses in minimal model Hamiltonians incorporating spin, charge, and lattice; (b) Understanding the subtle competitions among polarons at finite densities which determine their global mesoscopic patterns; and (c) Establishing useful signatures of particular mesoscopic polaron patterns so that they may be identified by appropriate combinations of experiments. In the brief space available here we concentrate on a representative example of (c). We note, however, that the issues of topic (a) arise from the internal structure of *composite* (spin-charge-lattice) polaron "particles" and can strongly influence issues such as polaron formation, transport, localization in disorder fields, and excited state and ultrafast spectroscopy.[3] Modeling and measuring these properties is increasingly critical to modern technology but in a poor state. Regarding topic (b), just as in crystals the forces determining mesoscopic polaron ordering (into gas, liquid, glass and solid phases) is typically a delicate balance of forces. In TMOs this combination of forces is certainly not universal, including long-range Coulomb and elastic fields, and short-range fields from spin, charge, orbital and lattice (e.g. Jahn-Teller) fluctuations coupled to the local but powerful polaronic disturbances. The experimental imaging of mesoscale patterns is in its infancy, and modeling of mesoscale ordering is likewise primitive.[4]

Tuning to topic (c), establishing useful signatures of polaron patterns, we report here an example of using *inhomogeneous (unrestricted) Hartree-Fock* (IHF) methods for layered TMOs, focusing on various "stripe" patterns of holes in antiferromagnetic (AF) backgrounds. Details of the method can be found in Ref. 5 and we have applied if to small polarons in a number of materials - linear chain charge-transfer mixed valence solids.[6] CuO_2 layers,[7] NiO_2 layers,[8] $La_2Cu_{0.5}Li_{0.5}O_4$,[9] and the 1- and 2- dimensional Anderson lattice model with electron-lattice coupling.[10] Some important general points emerge from all of those examples: (i) Small electron-lattice coupling can have a large local effect in the presence of doping, even for a strongly AF or charge-density-wave global undoped phase. Thus modeling must

include spin, charge and lattice degrees-of-freedom; (ii) Multiband effects are pronounced in the structure of small polarons, and in the non-homogeneous (e.g. long-period and glassy) phases which accompany the crossovers between different global broken-symmetries and between broken-symmetry and metallic phases. Thus, projecting into effective single bands must be treated with great caution. The advantage of using the IHF approximation is that it allows a systematic probe of a large parameter space and permits spatially inhomogeneous, lower energy ground states to be accessed and compared. Vertex corrections, often important in low-dimensional pure HF models of electron-electron interactions, are much less important in the presence of coexisting local lattice distortions. Having determined mesoscopic charge-ordered ground states, a numerical random phase approximation (RPA) then identifies spin, charge and lattice fluctuations, characteristic of a particular pattern - and accessible to appropriate experiments. Here it is important to note that: (i) Quite new energy scales can become active relative to globally homogeneous phases. For example, in the case of $La_2Cu_{0.5}Li_{0.5}O_4$ the eV scale "Zhang-Rice" singlet is dominated by a 0.1 eV scale magnetic excitation.[9] Again, new low-energy magnetic excitations become active at the "edge" of hole stripes[7,8] (see below). Similarly, lattice excitations ("phonons") develop totally new modes, which we term "local" phonon modes below; (ii) Just as in all polaron physics,[5,6] mesoscale charge-ordering is accompanied by new characteristic scales at both *high* and *low* energies. Electronic states appear in the global HF gap between filled and unfilled energy levels (intragap states responsible for "pseudogap" behavior) and are seen in optical absorption, resonant Raman, etc. Lattice vibrations, corresponding to shape oscillations of the mesoscale patterns, appear at phonon energies scales in infrared or Raman or magnetic spectroscopies. The *correlation* of those high- and low-energy signatures is a very distinctive label a particular mesoscale structure.

II. AN EXAMPLE: STRIPES IN THE 2-DIMENSIONAL, 3-BAND PEIERLS-HUBBARD MODEL

As an example of the philosophy and approach described in Section I, we briefly describes hole doping in a layer of CuO_2 and focus on various stripe patterns; complete details can be found in Ref. 7.

We use a two-dimensional three-band Peierls-Hubbard model, in which $d_{x^2-y^2}$ orbitals of Cu and $p_{x,y}$ of O are explicitly included, and moreover electron-phonon (e-ph) interactions are taken into account. The Hamiltonian of this model reads

$$\begin{aligned} H = & \sum_{i\neq j,\sigma} t_{ij}(\{u_k\}) c^\dagger_{i\sigma} c_{j\sigma} + \sum_{i,\sigma} \epsilon_i(\{u_k\}) c^\dagger_{i\sigma} c_{i\sigma} \\ & + \sum_i U_i c^\dagger_{i\uparrow} c^\dagger_{i\downarrow} c_{i\downarrow} c_{i\uparrow} + \sum_{\langle i\neq j\rangle,\sigma,\sigma'} U'_{ij} c^\dagger_{i\sigma} c^\dagger_{j\sigma'} c_{j\sigma'} c_{i\sigma} \\ & + \sum_l \frac{1}{2M_l} p_l^2 + \sum_{k,l} \frac{1}{2} K_{kl} u_k u_l, \end{aligned} \tag{1}$$

which has been successfully employed to study the polaron states in cuprates[5] and the unusual low-energy magnetic excitations in $La_2Cu_{0.5}Li_{0.5}O_4$.[9] Here $c^\dagger_{i\sigma}$ creates a hole with spin σ at site i in the $d_{x^2-y^2}$ or $p_{x,y}$ orbitals. For the lattice part, we study only the motion of O ions along the Cu-O bonds and assume, for simplicity, that only diagonal components of the spring-constant matrix are finite, $K_{kl} = \delta_{kl} K$. For electron-lattice couplings, we assume that the nearest-neighbor Cu-O hopping is modified by the O-ion displacement u_k as $t_{ij} = t_{pd} \pm \alpha u_k$, where the + (−) applies if the bond shrinks (stretches) with positive u_k. The Cu-site energy is assumed to be modulated by the O-ion displacement u_k linearly as $\epsilon_i = \epsilon_d + \beta \sum_\epsilon (\pm u_k)$, where the sum extends over the four surrounding O ions. Other forms of e-ph coupling can be easily included in our approach, as well as disorder and impurities. We include Hubbard repulsion on both Cu-site (U_d) and O-site (U_p) and the nearest-neighbor Cu-O Coulomb repulsion (U_{pd}).

Mean-field states were obtained by solving the Hamiltonian in an IHF approximation with self-consistent conditions for on-site and nearest-neighbor charge and spin densities, as

well as lattice displacements, without assumption on the form of these quantities.[5,6] Self-consistent nonlinear equations are obtained by minimizing the total energy with respect to these quantities, resulting in generally inhomogeneous patterns. We use periodic boundary conditions and the representative parameters are taken from local-density-approximation electronic estimates: $t_{pd} = 1$, $\Delta \equiv \epsilon_p - \epsilon_d = 4$, $U_d = 10$, $U_p = 3$, and $U_{pd} = 1$, $\alpha = 4.5/\text{Å}$, $\beta = 1/\text{Å}$, and $K = 32/\text{Å}^2$.[5] We choose the system in such a way that it consists of 5×4 CuO_2 unit cells for vertical stripes and 5×5 unit cells for diagonal stripes. Since the stripe is an antiphase antiferromagnetic domain wall, in such systems mismatch of spin in the boundary can be avoided. We add four extra holes to the stoichiometic state in the 5×4 system and five extra holes in the 5×5 system, leading to the same hole concentration, 0.2/unit cell.

As detailed in Ref. 7, *four* varieties of stripe patterns are found in this approach. Three are centered on Cu sites: *vertical*, *diagonal* and *zig-zag*. These have rather similar energies with the zig-zag gaining slightly more energy from distortion of the oxygens. Both vertical and diagonal stripe segments have been inferred from scattering experiments on doped transition metal oxides.[7,8] All of these stripes are characterized by real-space spin-charge phase separation; the added holes organize into the striped patterns; spin is quenched in the stripes and antiferromagnetically coupled elsewhere with a π phase shift across the stripe; and finally, due to the el-ph interactions and accumulation of charge in the stripe, the oxygens adjacent to the stripe experience strong lattice distortion, whereas other oxygens are undistorted. An example of a zig-zag stripe is shown in Fig. 1 (see Ref. 7 for other types). Of course patterns composed of combination of these various stripes are also metastable configurations, depending on parameters, doping density, and boundary conditions, so that a great variety of ultrafine scale phase separation patterns should be anticipated in oxide samples. A distinct additional stripe type is one centered on *oxygens* rather than metal sites. Such stripes have been suggested both in cuprates[7] and nickelates[8] and obtained by the present IHF approach–in the cuprates they are excellent candidates for the source of anomalous "$(\pi, 0)$" phonons reported in recent neutron scattering studies.[11]

Having obtained a mean field spin-charge-lattice stripe configuration, RPA analysis

can then be carried out numerically to obtain linear spectra of lattice, spin and charge fluctuations.[5] Regarding the "phonon" modes, the presence of stripes results in the loss of some modes from the phonon band of the homogeneous undoped situation, accompanied by new *localized* phonons in a band split from the continuum. The oxygen displacements in the eigenvectors for the localized modes, parallel and perpendicular to the stripes, will be valuable for experimentally distinguishing between stripe types in infrared, Raman or neutron scattering. An example of the phonon disportion predicted for a zig-zag stripe is shown in Fig. 2. The localized phonon band involves vibrations only of oxygens in the immediate neighborhood of the stripes. Very interestingly, low-energy *spin* excitations are also activated by the stripes. For example, the spectral weight $f(\mathbf{k},\omega) \propto \frac{\pi}{N_{\rm cell}} \sum_{n\neq 0} |\langle 0|\mathbf{S}^{\perp}_{\rm Cu}(\mathbf{k})|n\rangle|^2 \delta(\omega - (E_n - E_0))$ obtained for the zig-zag stripe of Figs. 1 and 2 is shown in Fig. 3 for k=(0,0). (Here $\mathbf{S}_{\rm Cu}(\mathbf{k}) = \sum_{i\in {\rm Cu}} \frac{1}{2} \sum_{\tau\tau'} c^{\dagger}_{i\tau}\sigma_{\tau\tau'}c_{i\tau'}$ and $N_{\rm cell}$ is the number of CuO_2 units.) Magnetic excitations ("localized spin waves") at the magnetic *edges* of the stripes appear at the low energies in Fig. 3 – substantially below the $\sim t_{pd}$ scales of the undoped case (not shown). These should be seen in NMR or inelastic neutron scattering. Interestingly, the new phonon and spin excitations are in rather similar energy ranges, pointing to the probability of novel magnetoelastic coupling around mesoscopic hole ordered patterns such as stripes. Spin excitations at other wavevectors are reported in Ref. 7, as are weaker-intensity charge fluctuations,

III. SUMMARY

It is becoming increasingly evident experimentally that phase separation into charge-rich and charge-poor nanoscale domains is typical of complex electronic materials and in particular hole-doped transition metal oxides. This intrinsically inhomogeneous property is very likely to be central to macroscopic functionalities (superconductivity, magnetoresistance, ferroelectricity, etc) and therefore it is extremely important to understand the origins and signatures of mesoscopic charge ordered patterns. We have suggested here that inhomoge-

neous (unrestricted) Hartree-Fock is a valuable modeling approach, and used it for a variety of model oxide[5,7–9] and f-electron[10] Hamiltonians. In particular, this scoping approach has demonstrated: (a) the need to couple spin, charge and lattice degrees-of-freedom to understand "small polarons" and their assemblies; (b) the need to include multiple bands (e.g. Cu and O orbitals) to adequatedly discriminate various types of mesoscale patterns (e.g. vertical and diagonal stripes, metal- and oxygen-centered stripes); (c)fluctuations in the presence of mesoscale polaron patterns (localized phonons, spin waves and charge excitations) which can serve to experimentally discriminate between different patterns; and (d)the need to correlate low- and high-energy signatures of polaron patterns, again to reliably discriminate between them.

Clearly much research remains, including adequate treatments of charge-order formation (competitions of long- and short-range and disorder forces), nonadiabatic effects, and multiscale dynamics (including quantum and thermal activation of mesoscopic stripe segments). We conclude with the speculation that the very fine scale electronic structure described here is intimately coupled to *elastic* fine scale structure in these kinds of complex electronic materials – structures observed is high-resolution microscopies[12] such as twinning and tweed, accompanying solid-solid structural phase transformations and characteristic of all transition metal oxides. In fact the *same* high sensitivities to small unit cell distortions which results in the local, directional "polarizability" driving polaron formation and ordering is also responsible for the coupling of inter- and intra unit cell lattice distortions responsible for long-range, directional elastic fields – flat Fermi surface regions result in large shear anisotropies and fine scale structural inhomogeneity in extensive temperature and pressure intervals around global structural transformations. This structural complexity extends to much larger mesoscopic scales than the small polaron scale. However, it is nucleated[13] by very local strong perturbations, including extrinsic disorder (e.g. impurities, pressure and concentration variations) *and* the *intrinsic* disorder represented by charge localization. Reciprocally, the anisotropic, long-range elastic interactions between charges are a key element controlling their ordering and dynamics. Exploring this interplay between structural and

electronic mesoscale inhomogeneities will certainly be an essential theme for future years, as we move toward understanding mesoscale complexity for predictive control of desired functionalities - electronic, magnetic, optical and structure, strength properties are intimately coupled.

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REFERENCES

[1] A. R. Bishop and H. Röder, Current Opinion in Solid State and Materials Science **2**, 244 (1997).

[2] See, e.g., articles by A. Bianconi *et al.* and T. Egami *et al.*, these Proceedings.

[3] M. Salkola *et al.*, Phys. Rev. B **51**, 8878 (1995); W. Z. Wang *et al.*, Phys. Rev. Lett. **80**, 3284 (1998), J Mustre de Leon *et al.*, these Proceedings; S. Trugman, these Proceedings.

[4] E.g., B. Stojković *et al.*, Los Alamos Preprint (1998).

[5] K. Yonemitsu, A. R. Bishop, and J. Lorenzana, Phys. Rev. Lett. **69**, 965 (1992); Phys. Rev. B **47**, 12059 (1993).

[6] I. Batistic *et al.*, Phys. Rev. B **44**, 2652 (1991); X. Z Huang and A. R. Bishop, Phys. Rev. B **48**, R16148 (1993).

[7] Z. G. Yu, J. Zang, J. T. Gammel, and A. R. Bishop, Phys. Rev. B **57**, R3241 (1998).

[8] Y. Yi *et al.*, Phys. Rev. B (1998).

[9] Z. G. Yu, A. R. Bishop, and J. T. Gammel, J. Phys. Conden. Matt. **10**, L437 (1998).

[10] Y. Yi, A. R. Bishop, and H. Röder, unpublished.

[11] See T. Egami, these Proceedings.

[12] E.g., B. Raveau, these Proceedings.

[13] T. Lookman *et al.*, Los Alamos Preprint (1998).

FIGURES

FIG. 1. Charge (radii of the circles) and spin (arrows) densities in the zig-zag stripe. The large circles are for Cu sites and small ones for O sites. The hole concentration is 0.2.

FIG. 2. Phonon dispersion in the zig-zag striped phase. Points represent specific eigen-modes and their strength is proportional to the density of the mode. Frequencies in cm^{-1}.

FIG. 3. Spectral weight of magnetic excitations in the zig-zag stripe.

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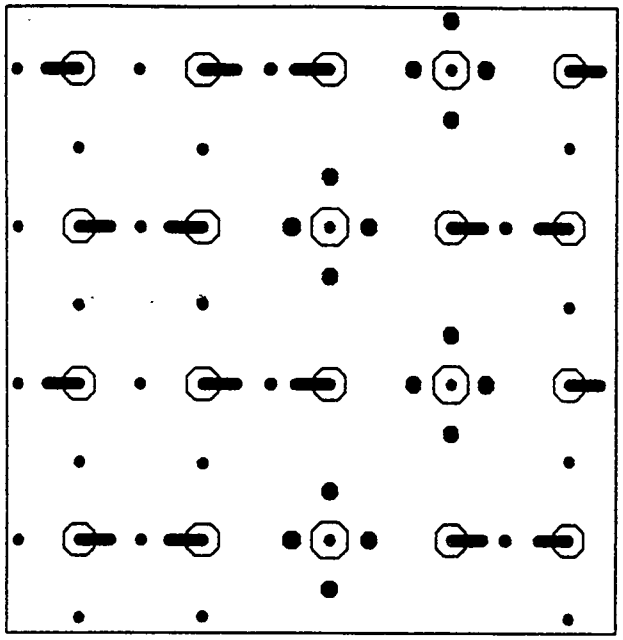

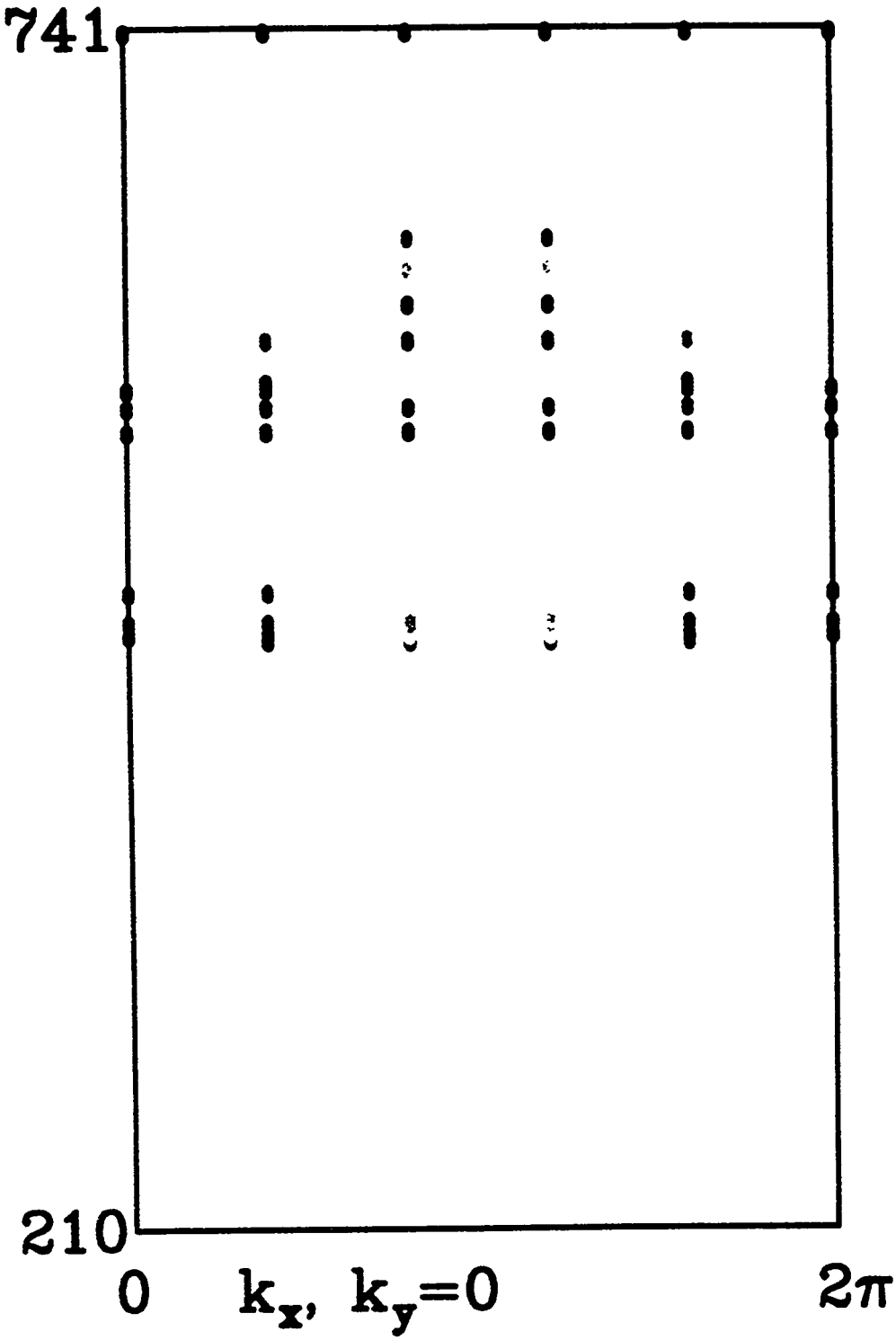
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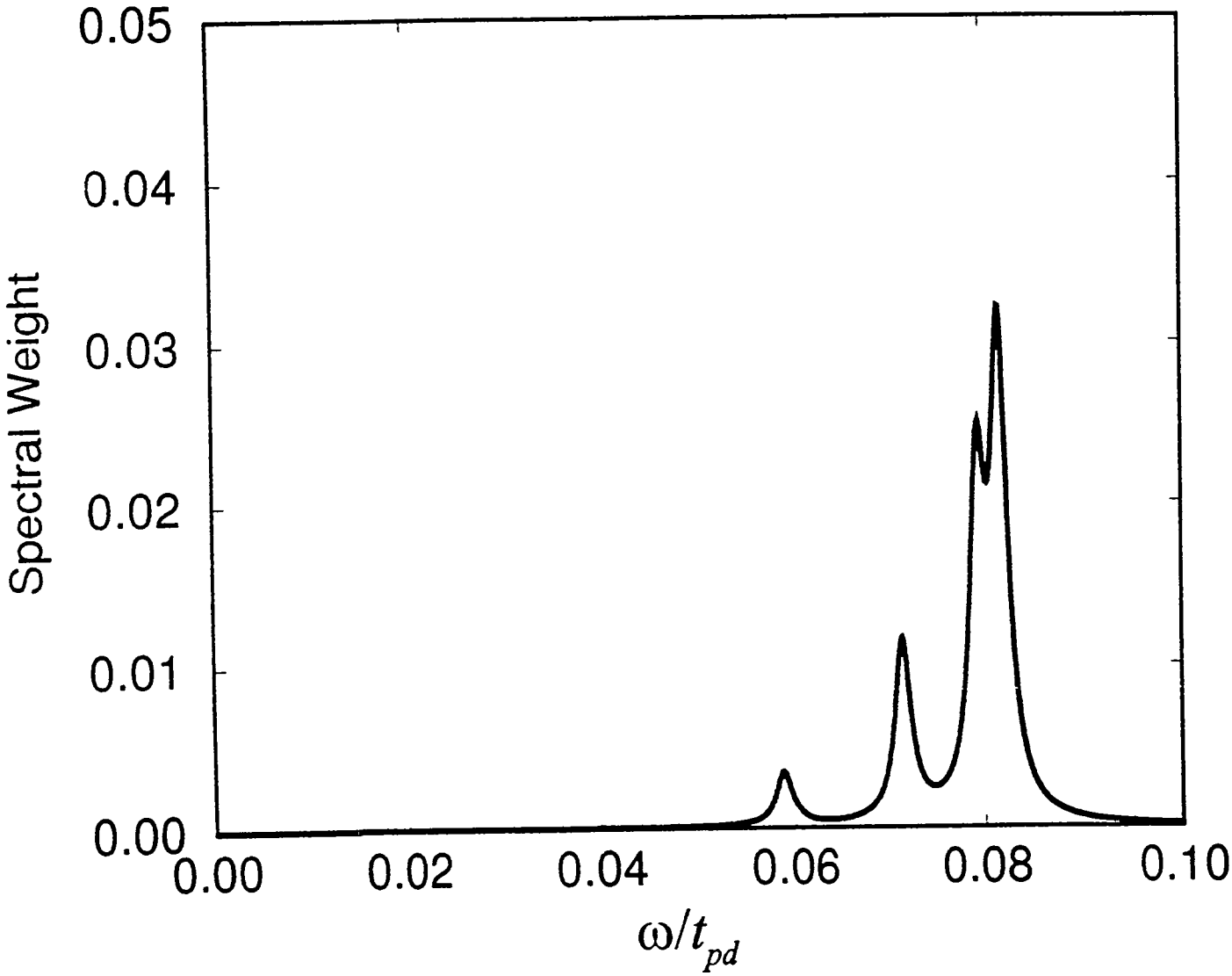
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