"half-filled" criterion and make it into a metal. From a "mean field" point of view, as soon as the system is metallized it becomes a superconductor, since the pairing already exists in the RVB state, and an energy $\sim J$ is required to break a valence-bonded pair. As shown in Fig. 1B, as soon as the occupancy leaves N, there is no cusp in the energy, the compressibility becomes finite, and by the standard arguments the state can acquire a fixed θ rather than n.

As a practical matter, the effective mass of quasiparticles will be of order $m^* = m/\delta$, where δ is the fractional doping $n = N(1 - \delta)$. Correspondingly, the coherence length ξ_0 will be of order

$$k_F\xi_0 = \frac{E_F}{\Delta} \ll 1$$

where k_F and E_F are the Fermi wave vector and energy, respectively, Δ is the energy gap, and the kinetic energy is of order $t\delta$. Thus the transition temperature T_c will at first be dominated by phase fluctuations. (In actual physical fact, at first the dopant ions will be screened out by bound quasiparticles, and it will take a finite dopant concentration to metallize the sample.) The maximum T_c, of order or less than $t^2/U = J$, will occur when $t/U \sim \delta$ and kinetic and pair-binding energies match. Pressure will increase t and, within limits, increase T_c as well.

From a theoretical point of view, the most exotic feature of these experimental results (*1*) is that they confirm the existence of a new liquid, only conjectured previously (*3, 5, 10*). This liquid is insulating only by virtue of a "commensurability gap," and therefore resembles the Laughlin state in the fractional quantum Hall effect (*15*). Both of these states may be described as "Mott liquids" since the basic physics is that of the "Mott transition" (*16*), and their key feature is that there is no symmetry breaking vis-à-vis the high-temperature state.

There are several experimental consequences of the above. The key point is the observation of the RVB state in the stoichiometric La_2CuO_4, which should be easy with neutrons, especially if there is a pseudo-Fermi surface. Second, the pseudo-Fermi surface may or may not cross the real Fermi surface, defining lines of zeroes of the gap function. The occurrence of lines of zeroes and of antiferromagnetic correlations in some heavy fermion superconductors suggests a family resemblance to the RVB state, although the parameter values are totally different.

Finally, I would call attention to the numerous unreproducible reports of high-temperature superconductivity in special samples of CuCl. In every case it is reasonable to imagine a surface layer of Cu^{2+} with or without the appropriate degree of oxidation; such reports should sharpen the search for still more RVB superconductors. It is also noteworthy that the first oxide superconductor, Li_2TiO_4 (*17*), closely resembles $NaTiO_2$, the only other likely RVB material.

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The Onshore Transport of an Oil Spill by Internal Waves

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Internal waves generated by tidal currents concentrated and transported an oil spill (liquid asphalt) onshore. Plankton net samples were collected in front of and behind a set of internal waves as well as in the convergence and divergence zones over the waves. Tar "balls" were most abundant (greater than 30-fold) in the samples from the convergence zone. Comparison of the abundance of tar balls in front of and behind the set of waves suggests that the internal waves "caught" about 68% of the asphalt encountered and concentrated and swept shoreward tar balls from almost 8 kilometers of ocean.

TIDAL CURRENTS FLOWING OFF THE continental shelf or across reefs or banks produce large internal waves (*1, 2*). Those waves formed at the shelf break propagate onshore (*3*). Surface currents over the waves produce alternating zones of convergence and divergence. Flotsam swept into the convergence, if buoyant enough, will be trapped there and carried onshore. Some types of larval invertebrates and fish migrate onshore by this mechanism (*4, 5*). Most oils float on water and potentially could be carried onshore by internal waves. This study shows that floating oil (spilled asphalt) was swept up by currents over a set of internal waves, concentrated in the convergence zones over the waves, and transported onshore. To my knowledge, this is the first time that onshore transport of an oil spill by internal waves has been observed and recognized, although it might be expected from the known properties of internal waves (*6*).

On 21 June 1985 a large (about 1.5×10^6 liters) tank of liquid asphalt burst at the Morehead City port in North Carolina (75°5'N, 35°4'W) (Fig. 1). Some of this asphalt spilled into the Beaufort Inlet and was carried out to sea by the tide.

Three days later surface plankton samples (from the top 26 cm of the water column) were collected with a Manta net (*7*) (26 by 96 cm, mouth opening; 0.333 mm, net mesh) from the waters around a set of internal waves (*8*). The set of internal waves was about 4 km offshore (Fig. 1). Replicate ($n = 3$) 5-minute tows (>50 m^3 of water filtered) were made in front of and behind

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the entire set of internal waves, in the convergence zones over the internal waves (*8*), and in the rippled water between convergence zones. The set of internal waves consisted of five, approximately 30-m-wide, strips of glassy water separated by about 100 m of rippled water. Flotsam had accumulated along the seaward edge of each glassy strip, indicating that these zones of smooth water were due to convergent currents over the internal waves. Samples were collected from the two most shoreward waves. Samples were preserved in Formalin, and in the laboratory, tar "balls" (0.1- to 75-mm irregularly shaped pancakes and globules of asphalt) were counted with the aid of a dissecting microscope. Because of the abundance of tar balls in the convergence zone samples, only an aliquot (1/10 of the volume) was examined, but the entire volume was examined in all other samples.

To test if the internal waves were causing onshore transport of buoyant flotsam, 50 surface drifters (Styrofoam cups weighted to float with their rims at the surface) were released in a line in front of and perpendicular to the set of internal waves. After 4 hours, 96% of the surface drifters were found in the convergence zone associated with the most shoreward internal wave of the set (Fig. 1), and they had been carried shoreward several kilometers. This set of internal waves was transporting flotsam shoreward.

The asphalt spill was relatively small and did not form a continuous oil slick. During the plankton tows, oil sheen (circular patches 1 to 2 m in diameter) and asphalt globules were only observed in the zones of glassy water. Numerous patches of asphalt were scattered throughout the convergence zones but tended to be concentrated near the seaward edge (Fig. 1). Tar balls were most abundant (>30-fold) in the plankton samples collected from the zones of glassy water (Fig. 2). The location of the abundant tar balls suggests that, as the internal waves propagated shoreward, scattered patches of asphalt were caught up in the convergence zones and carried shoreward. If this is true, then the concentration of asphalt in front of the set of internal waves must have been higher than that in the waters behind the set. The samples collected in front of and behind the set of internal waves were separated only by about 700 m, yet tar balls were significantly more abundant in front of the set than behind (Fig. 2, in front mean is 0.22 per square meter, SE is 0.07; behind mean is 0.07 per square meter, SE is 0.02; Wilcoxon's two-sample test, $P < 0.05$). The asphalt spill was concentrated and carried back shoreward by the internal waves. Internal waves can transport flotsam into the surf zone (*4, 9*). Hence, the asphalt in these slicks could have been deposited on the beach in less than 3 hours (assuming a wave speed of 35 cm/sec) (*10*).

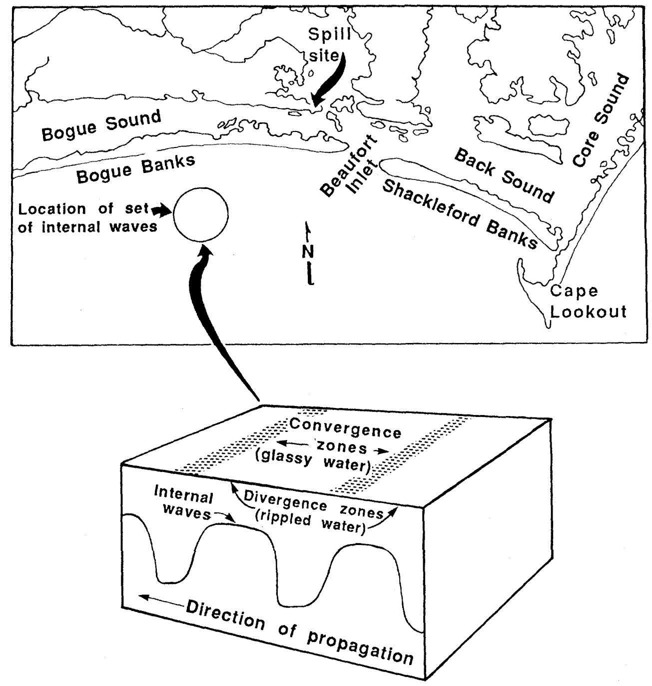

Fig. 1. Locations of the asphalt spill at the Morehead City port and the sampled set of internal waves. The inset shows the position of the convergence (glassy water) and divergence (rippled water) zones relative to the internal wave. Flotsam, the released surface drifters, and the spilled asphalt were most abundant in the convergence zones with the highest concentrations on the seaward side (to the right) of the bands of glassy water.

The data can be used to estimate the amount of onshore transport caused by the internal waves. If the five waves in the set were identical (that is, having a 30-m-wide convergence zone with 7.46 tar balls per square meter separated by 100 m of rippled water with 0 tar balls per square meter), then the total abundance of tar balls in a meter-wide swath through the set would be 1119. If the abundance of tar balls in the water "fished" by the internal waves was equal to that found in the waters in front of the set (that is, 0.22 per square meter) and the internal waves "caught" 68% of the tar balls encountered (*11*), then asphalt was concentrated and swept shoreward from about 8 km of ocean.

Movement of oil spills has been modeled by assuming that transport is due only to the combined forces of wind, currents, and, in coastal waters, the tides (*12, 13*). To my knowledge, the possibility that internal waves could transport oil spills has not previously been considered. Several factors may explain why this phenomenon has not been observed sooner. About half of the large and well-studied oil spills have occurred in winter because of storm-related shipwrecks. The water column is well mixed during this season, and because of the weak stratification, internal waves may have different characteristics or may be entirely absent. For example, Sawyer found that internal waves disappeared from Landsat photographs of the Mid-Atlantic Bight during the winter months (*10*). At the site of a large oil spill the surface of the ocean is often covered with a continuous slick. Such a slick might prevent an observer from seeing the alternating bands of glassy and rippled water that are characteristic of internal waves. Unless a researcher is specifically searching for the surface manifestations of internal waves, they can be easily overlooked.

Because tidally generated internal waves are ubiquitous over the continental shelves of the world (*14, 15*), onshore transport of spilled oil by internal waves potentially may occur along most coasts. Internal waves are not evenly distributed along shorelines (*10, 14, 15*). Some areas, because of offshore topography, are impinged upon by more internal waves than others (*10, 14*). Moreover, as the waves propagate shoreward they are refracted by the topography of the bottom of the ocean; they are concentrated to either side of submarine canyons and around headlands (*15*). Stretches of coastline where internal waves often impact may be more prone to contamination by oil spills. As has been suggested for Langmuir circulation

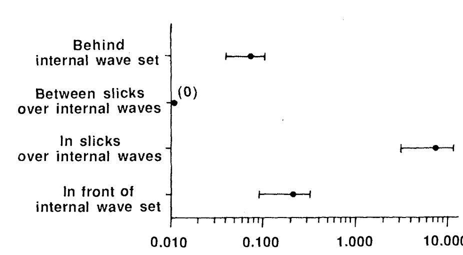

Fig. 2. The mean concentration (±95% confidence limits) of tar balls in the four habitats sampled. There were three replicates in each case.

(helical surface currents oriented downwind) (*16*), the downwelling currents at the convergence zone over internal waves may pull less buoyant fractions of an oil spill under water, making the spill inaccessible for cleanup operations. Finally, oil caught in the convergence zone could kill or injure (*17*) the larvae that are often concentrated there (*4, 5*).

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Aromatic Cross-Links in Insect Cuticle: Detection by Solid-State ^{13}C and ^{15}N NMR

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Cross-polarization magic-angle-spinning nuclear magnetic resonance spectroscopy has been used to determine insect cuticle composition and cross-link structure during sclerotization or tanning. Unsclerotized cuticle from newly ecdysed pupae of the tobacco hornworm, *Manduca sexta* L., had a high protein content with lesser amounts of lipid and chitin. Concentrations of chitin, protein, and catechol increased substantially as dehydration and sclerotization progressed. Analysis of intact cuticle specifically labeled with carbon-13 and nitrogen-15 revealed direct covalent linkages between ring nitrogens of protein histidyl residues and ring carbons derived from the catecholamine dopamine. This carbon-nitrogen adduct was present in chitin isolated from cuticle by alkaline extraction and is probably bound covalently to chitin. These data support the hypothesis that the stiffening of insect cuticle during sclerotization results primarily from the deposition of protein and chitin polymers and their cross-linking by quinonoid derivatives of catecholamines.

THE INSECT EXOSKELETON IS A COMplex extracellular cuticular structure whose chemical nature and physical properties vary with functional demands. It is composed primarily of protein, chitin, and water, the interactions of which, although poorly understood, largely determine structural and mechanical properties (*1*). During sclerotization (strengthening), the cuticle becomes stiffer, drier, and resistant to chemical and physical degradation. It has been proposed that catecholamines act as dehydrating agents, protein denaturants, and precursors of cross-linking agents for the presclerotized protein-chitin matrix (*2*). Proposed cross-linking intermediates include *o*-quinones or *p*-quinone methides, whose formation from catechols is catalyzed by oxidative enzymes in the newly secreted cuticle.

Because tanned cuticle is an intractable material and the putative cross-linking agent or agents are highly reactive and transient, the analytical techniques used in the past to study the chemistry of sclerotization have not yielded convincing proof for the cross-linked structures or proposed intermediates. However, recent studies of bacterial cell walls (*3*) have shown that the relatively new solid-state spectroscopic method, cross-polarization magic-angle-spinning (CPMAS) nuclear magnetic resonance (NMR) (*4*), makes it possible to evaluate cross-linked structures in intact biological tissue.

We report here the results of experiments in which CPMAS ^{13}C and ^{15}N NMR were used to determine in situ the relative concentrations of and covalent interactions among catecholamine, protein, and chitin in pupal cuticle of the tobacco hornworm, *Manduca sexta* L. The analytical method depends on the ability to identify and quantitate in intact cuticle the natural-abundance ^{13}C levels, as well as ^{13}C–^{15}N covalent bonds, between catechols or chitin labeled with ^{13}C and protein enriched in ^{15}N-histidine.

At ecdysis, *M. sexta* pupal cuticle is soft and colorless except for small tanned areas on the abdomen (*5*). In a few hours the cuticle stiffens and becomes dark brown. The natural-abundance ^{13}C CPMAS NMR spectra of cuticle can be used to estimate concentration changes of the major organic components during cuticular tanning or sclerotization (*6*). Protein carbons contribute to ^{13}C resonances (lines) 1, 2, 4, 5, and 10 to 16 (*7*) (Fig. 1C and Table 1). The broad peptide backbone α-carbon peaks between 55 and 62 parts per million (ppm) (lines 10 and 11) generally diagnose protein levels (*8*). The well-resolved sharp lines between 74 and 104 ppm (lines 6 to 9) are due to the 2-acetamido-2-deoxy-D-glucopyranoside (GlcNAc) carbons and so reflect chitin content. The oxygenated aromatic carbon

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