Stacked materials build up massive electrons

A heterostructure exhibits unusual electronic behavior previously seen only in materials with rare-earth or actinide elements.

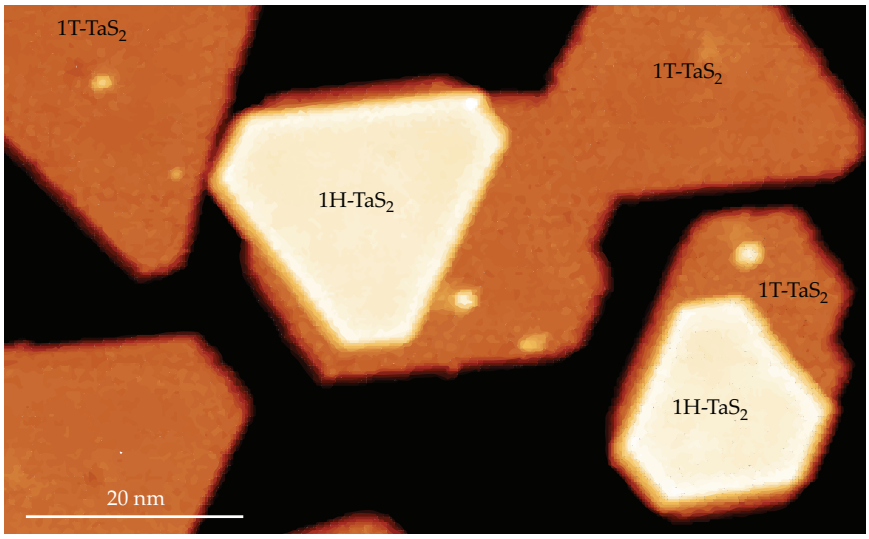

FIGURE 1. TANTALUM DISULFIDE grown by molecular-beam epitaxy forms two crystal structures, 1T and 1H. The random growth process creates three-atom-thick monolayer islands, shown in orange in this scanning tunneling microscopy image, and bilayer regions with the two layers taking the same or different crystal structures. The bright yellow regions are 1H-TaS_2 on 1T-TaS_2. Such heterostructures act as though their electronic behavior arises from charges of a mass that is one or two orders of magnitude larger than an electron mass. (Courtesy of Viliam Vaňo.)

As early as the 1930s, researchers began puzzling over an aspect of the electrical response in some nominally pure metals: At temperatures of a few kelvin, resistivity doesn't decrease with decreasing temperature, as they had come to expect; rather, it increases. Jun Kondo finally explained that behavior in 1964. The Kondo model describes an interaction between magnetic impurities in those metals and the conduction electrons. When the metal is sufficiently cooled, the scattering of conduction electrons increases because spin-exchange scattering with the impurities becomes possible.

About a decade after Kondo's initial work, Kenneth Wilson predicted that below a certain temperature, the coupling between the magnetic spins and conduction electrons is so strong that it quenches the localized spins, and the spins and electrons form a combined ground state known as the Kondo singlet. In the 1970s that so-called Kondo effect became widely studied in rare-earth compounds, with the role of magnetic impurities played instead by electron spins in the 4*f* and 5*f* orbitals of heavy ions in the materials.

A crystalline material's repeating spins create a lattice of Kondo singlets. In 1975 one such Kondo lattice in $CeAl_3$ was found to induce electronic behavior indicative of charge carriers more massive than those in most condensed-matter systems. Dozens of materials with rare-earth and actinide ions have since shown electrical responses indicating quasiparticles of an effective mass anywhere from 50 to 1000 electron masses. Those heavy fermions often give materials atypical electronic phases, such as multiple superconducting states (see PHYSICS TODAY, November 2021, page 19).

Now Peter Liljeroth and his colleagues at Aalto University in Finland have observed the formation of heavy fermions in a two-layer stack of tantalum disulfide, the first heavy-fermion material without rare-earth or actinide elements.[1] Their system is easy to make, handle, and tweak and potentially offers an accessible method to explore a wider range of heavy-fermion physics.

Happy accident

The Liljeroth group members stumbled on their heavy-fermion material by chance. They were originally growing TaS_2 to investigate whether it hosts a quantum spin liquid, a state whose unusual characteristic quasiparticles, known as spinons, have spin-½ but no charge. (For more on spin liquids, see the article by Takashi Imai and Young Lee, PHYSICS TODAY, August 2016, page 30.) Spinons are tricky to examine because they're chargeless, but the spatial pattern they adopt can conceivably be picked out with a scanning tunneling microscope or other probe.

Five years ago researchers found indications of a quantum spin liquid in bulk TaS_2, which has a layered structure of covalently bonded three-atom-thick layers weakly held together by van der Waals forces.[2] Because the influence of interlayer interactions complicated that observation, interest emerged in testing whether a single layer hosts a quantum spin liquid.

Liljeroth's chosen growth process, molecular-beam epitaxy, produces monolayer islands of TaS_2 with two possible crystal structures, denoted 1H and 1T. It also produces bilayer islands of the same layer structures and of differing structures: 1H stacked on 1T and vice versa, as shown in figure 1. Monolayer 1T-TaS_2 was what the researchers were after, but on a whim, Liljeroth's graduate student Viliam Vaňo also characterized the two heterostructure stacks with scanning tunneling microscopy and scanning tunneling spectroscopy (STS).

Vaňo saw the expected and established spectra for 1T and 1H monolayers. In heterostructures with a 1T layer on a 1H layer, an unexpected spectral spike, shown at the center of the top graph in figure 2, appeared periodically in scans over the sample. Those peaks were also recently observed in an independent study by Michael Crommie of the University of California, Berkeley, and his colleagues on a similar 1T-on-1H heterostructure of tantalum diselenide.[3] Their results, published a few months ago, include other measurements that indicate possible quantum spin liquid behavior in monolayer 1T-$TaSe_2$.

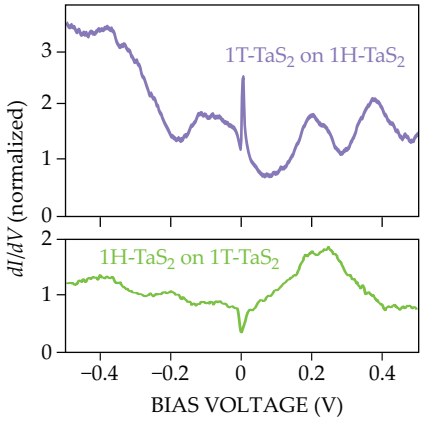

FIGURE 2. SCANNING TUNNELING SPECTRA of tantalum disulfide heterostructures reveal the heavy-fermion behavior of heterostructures of 1T-TaS_2 on 1H-TaS_2 and of 1H-TaS_2 on 1T-TaS_2. The change in tunneling current *I* relative to the applied bias voltage *V* indicates the number of electronic states at different energies for a given location on the sample. The measurements show a sharp peak at 0 V for one stacking order (purple) and a dip for the other (green). Those features taken together suggest that the material is showing electronic behavior that typically leads to unusual correlated states and that had previously been seen only in materials with rare-earth or actinide ions. (Adapted from ref. 1.)

For the 1H-TaS_2 on 1T-TaS_2 heterostructure, a dip appeared periodically in the tunneling spectrum, as shown at the center of the bottom graph in figure 2. Liljeroth's theory collaborator Jose Lado, also at Aalto University, proposed that the simplest explanation for the STS features—the spike in 1T on 1H and the dip in 1H on 1T—might be the formation of heavy fermions.

Measured response

STS measures the density of electronic states as a function of energy at single locations on a sample. At first, Liljeroth and his colleagues thought the spike in the 1T-on-1H measurements could be related to a previously observed cluster of states in bulk TaS_2 from a narrow electronic band near the Fermi level—the highest occupied energy level at zero temperature, or at a bias voltage of 0 V in STS measurements. But when they investigated how the peak responded to changes in temperature, its width didn't follow the thermal broadening that would be expected based on that explanation.

Instead, the spike's broadening with increased temperature suggested it was a manifestation of the Kondo effect. The associated Kondo lattice creates an intense peak in the local density of states near the Fermi level that grows as the material is cooled. Fitting the temperature dependence of Vaňo's measurements yielded 18 K as the Kondo temperature, above which the Kondo effect is negligible. What's more, an out-of-plane magnetic field broadened and eventually split the peak, an indication of the expected Zeeman splitting for a Kondo resonance.

The dip in the spectrum of 1H-on-1T heterostructures could conceivably arise for several reasons. One possible explanation is repulsive Coulomb interactions between quasiparticles. When quasiparticles are trapped in an island, their efforts to maximally avoid one another within those confines could lead to an energy gap in the material's electronic states and thus a dip in the STS measurement. Those Coulomb interactions would be stronger for laterally smaller heterostructures, but the researchers didn't see any size dependence for their spectral dip.

Other phenomena can create a gap in a material's electronic states. But as Liljeroth and his colleagues investigated them one by one, they found that the temperature and magnetic field dependence of the spectra didn't track with what's expected in those cases. The trends of the spectral dip did, however, agree with previous studies of heavy-fermion materials.

The STS spike and dip appeared in all the 1T-on-1H and 1H-on-1T heterostructures, respectively. What's more, because of the low disorder in the epitaxially grown TaS_2 layers, the features were more uniform across the sample than is typically the case in conventional heavy-fermion materials.

Stacking up

The two TaS_2 layers provide the necessary ingredients to form artificial heavy fermions. In conventional heavy-fermion systems, a single material, such as uranium ditelluride, provides the requisite conduction electrons and magnetic moments, from the electron spins in the 4*f* and 5*f* orbitals of its rare-earth or actinide ions. In Liljeroth's heterostructure, each layer provides one component. The 1T layer harbors a charge-density wave, which results in the atoms clustering into a repeating Star-of-David-shaped pattern. Each star hosts a magnetic moment from one unbonded orbital at its center, which serves the role filled by *f* electrons in conventional heavy-fermion materials. And metallic 1H adds conduction electrons, which hybridize with the magnetic moments to form a Kondo lattice.

Compared with conventional heavy-fermion materials, the heterostructure offers more avenues for tunability. For example, the relative angle of the layer lattices, the specific materials of those layers, and the magnitude of an applied electric gate voltage could all be adjusted. In the future, Liljeroth and his colleagues plan to chart the heterostructure's phase diagram, which should include a bevy of exotic phases observed so far only in rare-earth and actinide compounds.

Heavy-fermion materials are expected to show quantum criticality (see the article by Subir Sachdev and Bernhard Keimer, PHYSICS TODAY, February 2011, page 29). In a phase diagram, the quantum critical point is a precarious spot of instability near zero temperature between stable states that have transitions driven by quantum fluctuations. The materials often manifest unconventional superconductivity, which doesn't follow the Bardeen-Cooper-Schrieffer theory. Heavy-fermion superconductivity is of interest because it's highly unconventional and in some instances even topological, which means the behavior arises from the connectedness of the band structure rather than from its symmetry.

The Liljeroth group's results are part of a recent trend of using stacked two-dimensional metals, semimetals, semiconductors, and insulators to create new electronic and optical behaviors. (See the article by Pulickel Ajayan, Philip Kim, and Kaustav Banerjee, PHYSICS TODAY, September 2016, page 38, and PHYSICS TODAY, January 2020, page 18.) Materials in those structures include graphene, hexagonal boron nitride, and transition-metal dichalcogenides, such as molybdenum disulfide and TaS_2. Different layers can be assembled in various orders and combinations and at different angles to create any number of electronic and optical properties, including superconductivity, topological currents, and efficient photovoltaic responses.

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References

1. V. Vaňo et al., *Nature* **599**, 582 (2021).
2. M. Klanjšek et al., *Nat. Phys.* **13**, 1130 (2017).
3. W. Ruan et al., *Nat. Phys.* **17**, 1154 (2021).