

## AN ELECTRONIC VIEW OF DIAMOND

### ACHIEVING A MATCH BETWEEN THEORY AND EXPERIMENT

The foundation for calculating many of the large-scale properties of a solid, whether a structural steel alloy or a semiconductor computer chip, consists of a theoretical model for the behavior of electrons, particularly the valence electrons, whose accuracy can be validated experimentally. Rather than being localized around the atomic nuclei, the valence electrons in the chemical bonds that hold solid materials together travel throughout the volume of a sample. Theorists label each of the delocalized electrons with a momentum (technically, crystal momentum) and an energy. When plotted on a graph, the closely spaced momentum and energy values form continuous structures called valence bands.

#### THE VALENCE BAND WIDTH

The difference between the maximum and minimum electron energies in the valence band (band width) may be the single most important energy band parameter. For example, when the band width is small compared to the energy associated with electrostatic repulsion between neighboring negatively charged electrons, each electron tends to localize around one atom, because this is the easiest way for the electrons to avoid each other. Some of the most interesting materials today, including magnetic materials that are candidates for use in future computer data storage systems, fall in this category and have electrons that straddle the boundary between localized and delocalized behavior. The theory for such materials is not well established, and its development will require reliable experimental methods to measure key parameters.

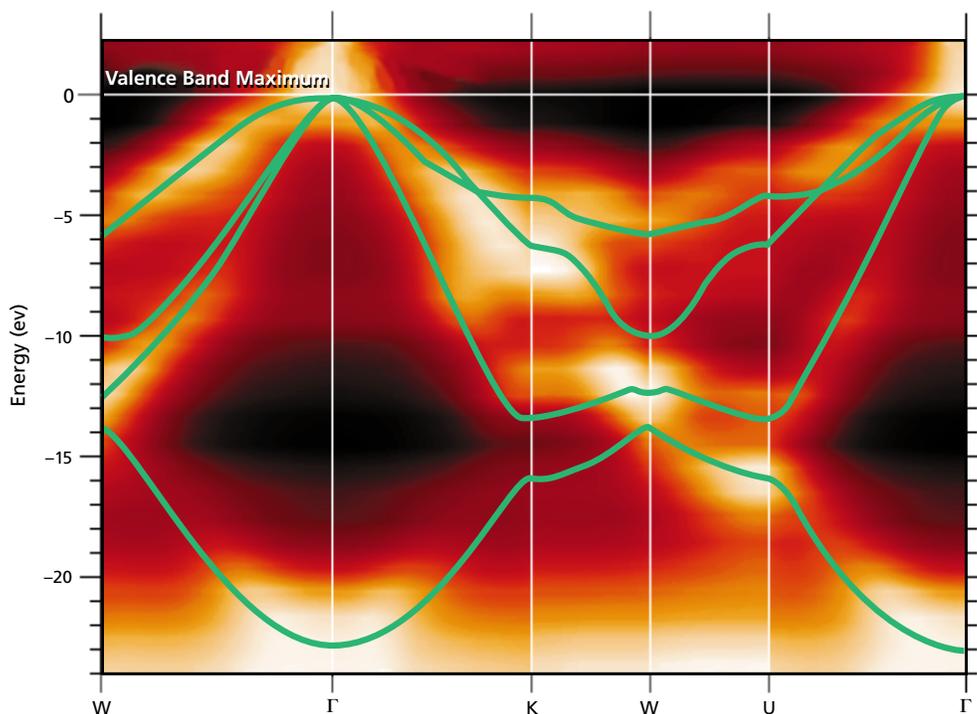
One such tool is photoelectron spectroscopy, which uses ultraviolet and long-wavelength (soft) x rays to excite valence electrons to higher energy bands from which they can travel to the surface and escape. By varying the wavelength (energy) of

the light, experimenters can selectively sample valence electrons with different energies (constant-final-state photoelectron spectroscopy). The direction of the photoelectrons (angle-resolved photoelectron spectroscopy) provides information about their momentum distributions. Combining this information displays the energy-momentum relationship (band structure).

#### QUASI-PARTICLES

In the conventional band model, theorists regard each electron as behaving independently of other electrons. This is called the one-electron approximation. While often useful, this approximation breaks down in many cases in which electrons appear to act in concert. Angle-resolved photoemission is a case in point. The problem is that the excitation of a valence electron leaves an empty state or hole in the valence band, which is effectively positively charged relative to the filled band. The resulting redistribution of electrons around the hole and the excited electron forms a “quasi-particle” which affects the energy of all electronic states and must be considered to make accurate calculations. A quasi-particle is an example of a many-body effect in which electrons do not act independently. It is the quasi-particle energies rather than the one-electron energies that photoelectron spectroscopy measures.

With this point in mind, researchers at the ALS using angle-resolved photoelectron spectroscopy have reported the first quantitative experimental verification of the valence-band structure of diamond. The experiments confirmed the quasi-particle model for diamond. In particular, they showed that the energy band width agreed with quasi-particle calculations by two different research groups but disagreed with one-electron calculations, which predicted band widths significantly smaller than measured.



The diagram shows the valence-band structure for diamond for different momentum directions, designated by letters at the bottom representing points of symmetry. The energy scale is relative to the top of the valence band. The calculated quasi-particle band structure is shown in green; the angle-resolved photoelectron spectroscopy data are shown in shades of orange and white, with lighter colors representing higher detected electron intensities. The horizontal axis shows crystal momentum. The experimental and theoretical data shown here are in excellent agreement for the characteristics modeled by the theory.

Collecting the large quantity of data required for accurate band mapping was aided by the use of a large area detector (display analyzer or ellipsoidal mirror analyzer). This device images photoelectrons emitted into an 84-degree cone around the sample on an electronic channel-plate detector, thereby preserving angular information while recording the electrons emerging from the surface. This approach, combined with the high brightness of the ALS, allows momentum distributions to be recorded in only a few seconds for each energy.

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