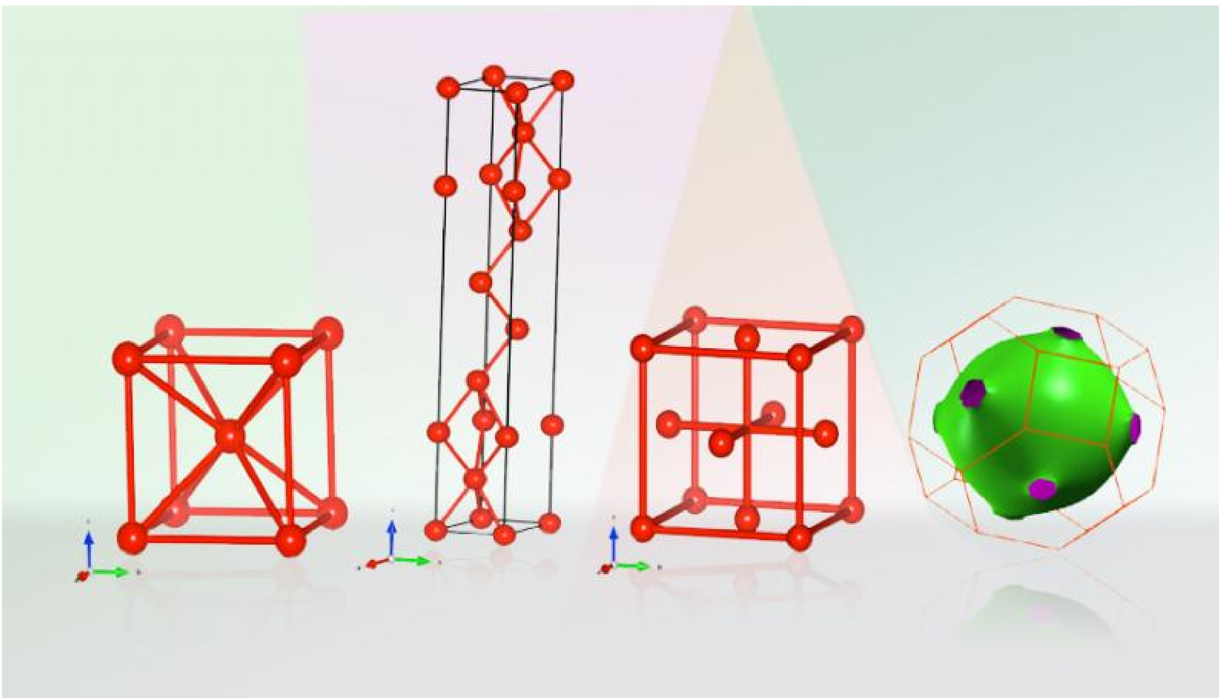
Peering at the crystal structure of lithium

June 23 2017



At ambient pressure and temperate conditions, lithium (Li) crystallizes in the cubic structure above (left). Upon cooling, it undergoes a transformation when it reaches about 80 K. The low-temperature structure was identified as having nine hexagonal stacking layers (middle-left). Traditional crystallographic methods have difficulty distinguishing it from other close-packed structures, such as the hexagonal lattice (middle-right) in a disordered polytype. The new LLNL study shows that measurements of the shape of the surface (right) of Li can be used to identify its crystalline structure. Credit: Lawrence Livermore National Laboratory

Elemental metals usually form simple, close-packed crystalline structures. Though lithium (Li) is considered a typical simple metal, its crystal structure at ambient pressure and low temperature remains unknown.

Lawrence Livermore National Laboratory (LLNL) researchers recently came up with a technique to obtain structural information for Li at conditions where traditional crystallographic methods are insufficient. Using this methodology, a decades-long puzzle finally may be solved.

Li is the lightest metal and least dense solid element at ambient conditions. Li and its compounds have several industrial applications, including heat-resistant glass and ceramics, lithium grease lubricants, flux additives for iron, steel and aluminum production, lithium batteries and lithium-ion batteries. These uses consume more than three quarters of lithium production.

"The superconductivity of alkali metals, and Li, is an issue that has been debated for many years," said Stanimir Bonev, LLNL lead author of a paper appearing in a recent edition of *Proceedings of the National Academy of Sciences*. "Only recently superconductivity in Li at ambient pressure was observed. But to understand the superconducting properties, it is essential to know the crystal structure."

As a complement to crystallographic methods, the LLNL team proposed measurements of the oscillations of the crystal magnetic moment in an external magnetic field. The team performed theoretical analysis showing that the spectrum of oscillation resonances is quite distinctive for different Li structures. A comparison with existing experimental data indicates that the low temperature phase of Li is incompatible with the previously assigned 9R (nine hexagonal stacking layers) structure.

Li has very interesting properties at high pressure. When it is compressed at low temperature, its superconducting critical temperature increases—from 0.4 millikelvin at ambient pressure to 20 kelvins at around 500,000 atmospheres of pressure. Then it transforms to a semi-conductor, then again to a metal at higher pressure, but with a very complex structure.

For years, scientists have tried to understand lithium's strange behavior. Theoretically, there are several structures that are very close in energy. To determine conclusively which among them has the absolute lowest energy, and is therefore the equilibrium structure, requires enormous precision in the calculations. At the same time, because of its light atomic mass, the dynamics of Li atoms is significant even at low temperature and this makes achieving such precision even harder.

On the experimental side—because Li is a low-Z element—it has a relatively weak response to X-rays and neutrons, which are the traditional methods to determine crystal structure. The transition to the low-temperature phase is gradual and it also breaks the single crystal sample.

In a polycrystalline sample, it is possible to have a mixture of several phases. As a result, scattering (X-ray and neutron) measurements can and have been interpreted in different ways.

"It is hard to identify conclusively what the structure is with these other methods alone," Bonev said. "There are only a few well pronounced diffraction peaks and they match several different structures. The measurements of course become harder at high pressure. With the method we propose, these difficulties are circumvented."

The research appears in the May 23 edition of *PNAS*.

More information: Sabri F. Elatresh et al. Evidence from Fermi

surface analysis for the low-temperature structure of lithium, *Proceedings of the National Academy of Sciences* (2017). DOI: 10.1073/pnas.1701994114

Provided by Lawrence Livermore National Laboratory