Researchers discover symmetry-breaking phase transitions after isotopic doping

June 2 2020, by Zhang Nannan

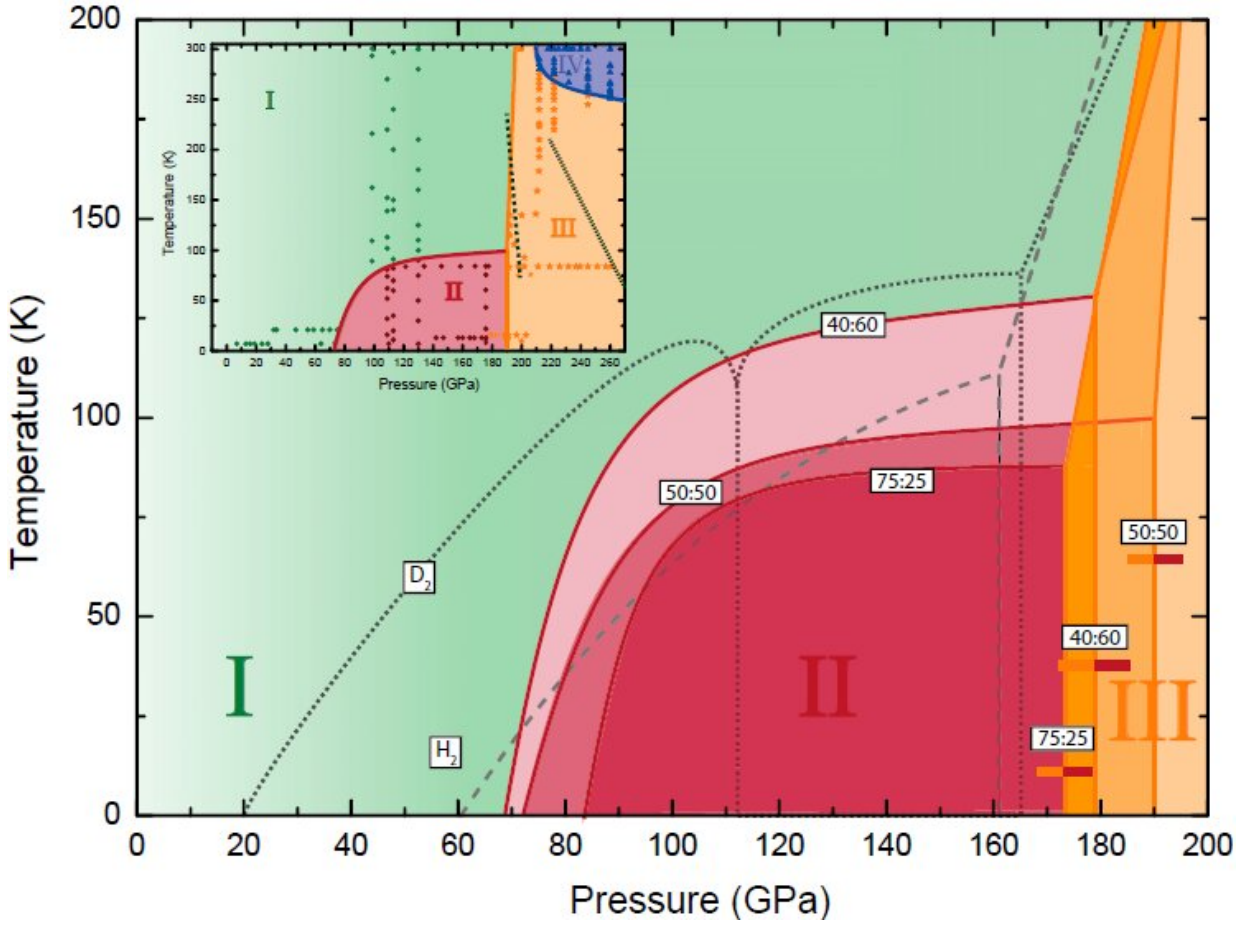

Figure 1. Proposed low-temperature phase diagrams of three representative H2–D2 mixtures (H_2:D_2 ratios of 75:25 = 3:1, 50:50 = 1:1, and 40:60 = 2:3). Phase I is shown in green, phase II is shown in red, and phase III is shown in orange. Different shades of color in phase II and phase III represent different mixture concentrations. The gray dashed lines represent the phase boundaries of the pure isotopes. (Inset) Extended phase diagram of the individual 50:50

mixture, showing collected data points for isothermal compression and isobaric cooling cycles. Credit: LIU Xiaodi

A joint team, while exploring phase diagrams in dense H_2–HD–D_2 mixtures, has reported a new discovery in which they found counterintuitive effects of isotopic doping on the phase diagram of H_2–HD–D_2 molecular alloy.

This work was conducted by a research team at the Institute of Solid State Physics, Hefei Institutes of Physical Science collaborating with researchers from the Center for High Pressure Science & Technology Advanced Research and University of Edinburgh. It was published in *PNAS* on 2 June 2020.

Molecular hydrogen forms the archetypical quantum solid. Its quantum nature is revealed by classically impossible behavior as well as by very strong isotope effects. Isotope effects between H_2, D_2, and HD molecules come from mass difference and the different quantum exchange effects: Fermionic H_2 molecules have antisymmetric wavefunctions, while bosonic D_2 molecules have symmetric wavefunctions, and HD molecules have no exchange symmetry.

To investigate how the phase diagram depends on quantum-nuclear effects, the joint team used high-pressure and low-temperature in situ Raman spectroscopy to map out the phase diagrams of H_2–HD–D_2 with various isotope concentrations over a wide P-T range.

When hydrogen and deuterium were mixed, they formed H_2 + HD + D_2 mixtures at very low pressures and room temperature.

They found that mixtures of H_2, HD, and D_2 behaved as an isotopic

molecular alloy (ideal solution) and exhibited symmetry-breaking phase transitions between phases I and II and phase III.

In their experiment, the researchers were surprised to find that all transitions occurred at higher pressures for the alloys than for either pure H_2 or D_2. This ran counter to any quantum effects based on isotope mass but could be explained by quantum trapping of high-kinetic energy states by the exchange interaction.

"Since HD has an intermediate mass and prevalent component in these alloys, one would expect that with its addition phase transitions would occur at intermediate P-T regimes," said the leading scientist of this study, "The discrepancy from the more classical understanding of molecular phase diagrams, derives from the quantum nature of the hydrogen molecules themselves, where the exchange-symmetry can in effect trap the molecules in different, higher energy states."

"HD molecules have no exchange symmetry, at low temperature all HD molecules will be in the lowest energy state. However, pure H_2 and D_2 have exchange symmetry, so some of the molecules would be trapped in the higher energy states. So the trapped kinetic energy is lower in mixtures than in either pure elements, and it shifts the phase transition to higher pressure in mixtures," said Liu Xiaodi, the first author of the paper.

More information: Xiao-Di Liu et al. Counterintuitive effects of isotopic doping on the phase diagram of H2–HD–D2 molecular alloy, *Proceedings of the National Academy of Sciences* (2020). DOI: 10.1073/pnas.2001128117

Provided by Chinese Academy of Sciences