Metallization of Solid Oxygen: Optical Gap Closure and Structural Evolution up to 100 GPa

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Abstract
Solid oxygen occupies a unique place among molecular solids because of the interplay between van der Waals interactions and the spin S=1 magnetic moment carried by the O2 molecule. This competition gives rise to a remarkably rich pressure–temperature phase diagram. Above 10 GPa, oxygen transforms into the ε-phase [1], a monoclinic C2/m structure composed of layered $(O_2)_4$ molecular clusters [2,3]. Compression progressively suppresses the magnetic degrees of freedom [4,5] and eventually drives an insulator-to-metal transition near 96 GPa [6,7]. Although metallic oxygen was discovered more than three decades ago, the microscopic mechanism of metallization and the structural nature of the metallic ζ-phase remain unclear.

To investigate this transition, we performed infrared absorption spectroscopy at 20 K and 300 K, up to metallization, complemented by Raman spectroscopy and high-pressure single-crystal x-ray diffraction. Raman measurements show no evidence of a structural phase transition between 20 K and 300 K throughout the stability domain of the ε-phase. Infrared absorption measurements reveal a continuous reduction of the optical gap with pressure. Analysis of the absorption edge indicates that an indirect gap closes near 85 GPa, while a finite direct gap persists up to the metallization pressure. The metallic state emerges through the collapse of this direct gap at 96 GPa.

The use of highly hydrostatic conditions and high-quality single crystals allowed us to determine the evolution of the atomic positions up to 101 GPa, extending previous structural studies into the megabar regime. We find that the layered arrangement of $(O_2)_4$ clusters remains essentially preserved up to metallization. The indirect gap closure produces no detectable structural signature, whereas the collapse of the direct gap is accompanied by a lattice instability leading to the ε-to-ζ transition. Structural refinements indicate that the metallic state retains a strongly layered character, suggesting that charge delocalization develops primarily within the molecular planes and that ζ-oxygen may constitute a highly anisotropic, quasi-two-dimensional molecular metal.

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