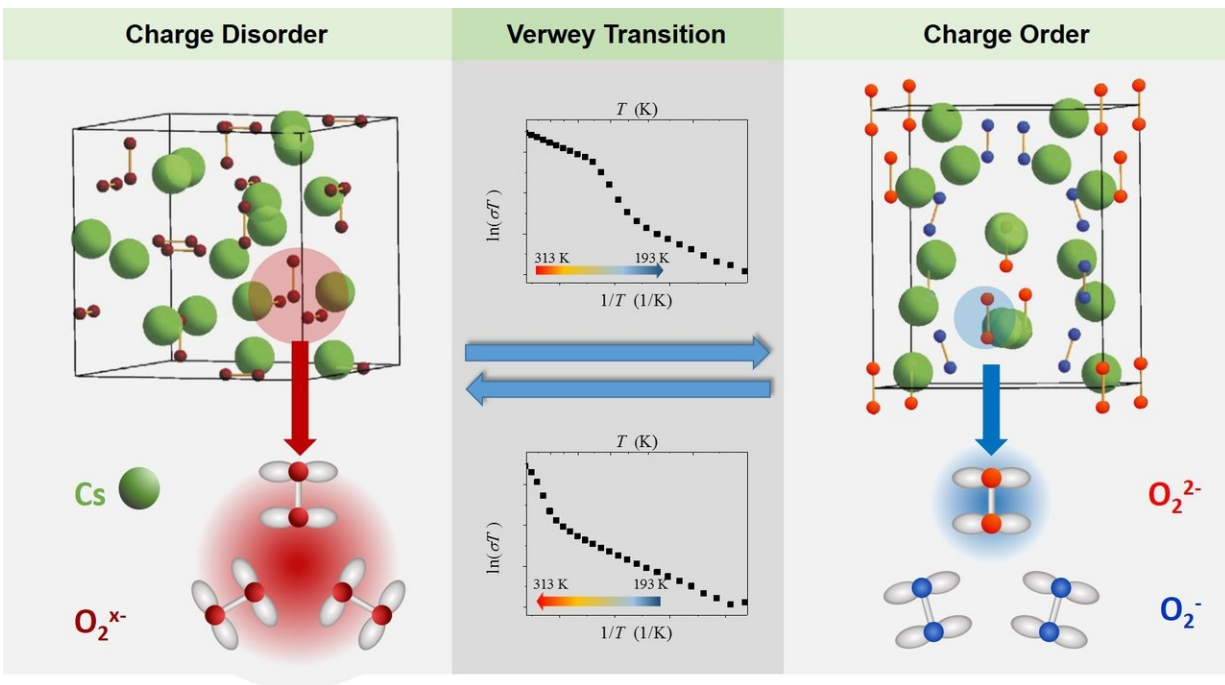


# Charge order and electron localization in a molecule-based solid

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The charge disordered crystal structure (left) where all negatively charged oxygen molecules are equivalent is transformed into the charge ordered structure (right) with distinct singly charged O<sub>2</sub><sup>-</sup> and doubly charged O<sub>2</sub><sup>2-</sup> ions. The transition is accompanied by a drastic drop or increase in the electrical conductivity (inverse of resistivity)  $\sigma$  on cooling or heating, respectively. The change in conductivity, shown here on a logarithmic scale, reveals a hysteresis. Credit: MPI CPfS

Charge ordering in mixed-valence compounds, which usually contain positively charged cations in more than one formal charge state, is of crucial importance for materials science. Many functional properties of materials like magnetism, magnetoresistance, ionic conductivity and superconductivity are found in mixed valence compounds.

One of the very first attempts to understand the mechanism of a charge ordering transition dates back to 1939 when Evert Verwey, a Dutch chemist, observed a sudden jump in resistivity in the prototypic mixed valence compound magnetite,  $\text{Fe}_3\text{O}_4$ , near  $-150^\circ\text{C}$ . He proposed that in the nearly metallic state of  $\text{Fe}_3\text{O}_4$  at temperatures higher than  $-150^\circ\text{C}$ , certain iron atoms are indistinguishable in the crystal lattice due to a full delocalization of charges. However, below this temperature a semiconducting state with a complex ordering pattern of charges over the available iron sites was established. In general, a transition from a charge-disordered into a charge-ordered state which is accompanied by a jump in electrical resistivity is nowadays called Verwey transition.

In the journal *Science Advances* now a research team of scientists from Germany and Slovenia reports a Verwey-type transition in a completely different class of mixed-valence [compounds](#) which is composed of negatively charged dioxygen molecules. The cesium compound  $\text{Cs}_4\text{O}_6$  undergoes a phase transition from a state with indistinguishable molecular  $\text{O}_2^{x-}$  entities to a state with well-defined singly charged superoxide  $\text{O}_2^-$  and doubly charged peroxide  $\text{O}_2^{2-}$  anions, which is accompanied by a corresponding change in charge transport dynamics. These results are supposed to shed new light on the mechanism of Verwey-type charge ordering phenomena.

"The Verwey-type transition in the cesium oxide  $\text{Cs}_4\text{O}_6$  is conceptually more simple than the original one in  $\text{Fe}_3\text{O}_4$ " [states](#) Peter Adler, the first author of the study. Whereas in  $\text{Fe}_3\text{O}_4$  the charge order state is complex and it is difficult to identify individual charge states the situation is more

unambiguous in  $\text{Cs}_4\text{O}_6$  as the molecular entities in the charge ordered state reveal the typical structural and magnetic features of the constituting paramagnetic superoxide and diamagnetic peroxide units. The authors have established the properties of  $\text{Cs}_4\text{O}_6$  by using several experimental techniques, namely neutron diffraction for the study of the crystal structure as well several spectroscopic techniques for verifying a charge localization transition which is a typical hallmark for Verwey-type charge ordering processes. By contrast to  $\text{Fe}_3\text{O}_4$  the present compound  $\text{Cs}_4\text{O}_6$  remains magnetically disordered down to a temperature of  $-271^\circ\text{C}$  which is only two degrees above the absolute zero point and it is much less conducting than  $\text{Fe}_3\text{O}_4$ . The molecular nature of the basic building units and the peculiar features of  $\text{Cs}_4\text{O}_6$  should be favorable for disentangling the complex interplay of the charge, spin, and lattice contributions to Verwey-type charge ordering phenomena. The intertwining of the different degrees of freedom may in the future even be used to control new materials functionalities through the Verwey transition.

Contemporary examples for functional materials properties related to mixed-valence are high-temperature superconductivity in copper oxide-based superconductors where the superconducting state competes with a magnetic and charge order state or very large ("colossal") magnetoresistance effects in certain manganese oxides which occur in the vicinity of a transition from a delocalized to a more localized mixed-valence state. Accordingly, unravelling the mechanism of charge ordering processes in mixed-valence compounds is an important subject in materials science. The breakthrough of the present study is the observation of such charge ordering in a relatively simple crystal structure where novel physical phenomena is expected to emerge from intertwining of degrees of freedom pertinent to the well-defined electronically active oxygen molecular units.

**More information:** "Verwey-type charge ordering transition in an

open-shell p-electron compound" *Science Advances* (2018).  
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