

Nuclear Physics for research on the mechanism of the Verwey transition in magnetite, and the W. Kołos Award in chemistry to Assoc. Prof. Wojciech Dzwolak from the University of Warsaw and the Institute of High Pressure Physics for papers on the

thermodynamics and structural aspects of protein aggregates with an emphasis on chiral bifurcation.

Various members and employees of the Division earned numerous honors and distinctions in 2008 for outstanding achievements in science.

## Verwey transition in magnetite: Cooperative electron-phonon scenario

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Magnetite ( $\text{Fe}_3\text{O}_4$ ), known also as lodestone, was already discovered back in ancient Greece and its extraordinary magnetic properties have fascinated people throughout the history of physics. More than 70 years ago, a puzzling new phenomenon, a phase transition with a characteristic jump in electric conductivity at  $T_c = 121$  K, was observed by Verwey. In spite of intensive research, a microscopic theory of the Verwey transition long remained out of reach and only during recent years has a coherent picture of this phenomenon emerged. Our theoretical work has solved many problems associated with the Verwey transition and substantially contributed to the current understanding of its mechanism.

The theoretical description of electron systems is based on two fundamental and mutually exclusive ideas. One is the idea of weakly interacting electrons, lying at the heart of single-electron approaches such as the Fermi liquid theory of metals and the density-functional theory, providing a basis for the band structure calculations and related *ab initio* methods. The other basic idea connects the insulating behavior of many compounds, e.g. the transition-metal oxides, with strong electron Coulomb interactions. A possible transition between a metallic and insulating state, driven by the local electron interactions, was first put forward by Mott and became one of the most fascinating phenomena in solid state physics.

The mechanism of a phase transition usually involves a breaking of the symmetry of one phase and the appearance of an order parameter in the other, low-symmetry phase. There are two main concepts of the Verwey transition, which assume different mechanisms of symmetry breaking. According to Verwey's original idea, the conductivity in magnetite decreases due to electron localization and charge

ordering on iron atoms. In this model, the distribution of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions, stabilized by the long-range Coulomb interactions, breaks the symmetry of the high-temperature metallic phase. However, diffraction measurements of the crystal structure at low temperatures did not confirm such an ionic order, pointing instead to a rather different scenario. It assumes that the phase transition is driven by atomic displacements, which breaks the cubic symmetry ( $Fd3m$ ) and induces the monoclinic phase ( $P2/c$ ). The structural instability would correspond to a condensation of some phonon mode with a simultaneous change of the electronic properties. No soft mode, however, was detected and a standard phonon mechanism of the Verwey transition was questioned.

Our studies used the density-functional theory to determine the electronic, structural, and dynamical properties of magnetite. The on-site Hubbard interaction  $U$  between electrons in the  $3d$  states on iron was included in the  $\text{LDA}+U$  approximation. Focusing on the effect of phonons on the crystal and electron structure, we discovered that the nature of the electron-phonon coupling changes radically, when these local electron correlations are taken into account. For a realistic value of  $U = 4$  eV, the phonon mode with the  $X_3$  symmetry strongly couples to electrons, lowering the energy of the system and generating the gap in the electron density of states (see Fig. 1). Thus, the  $X_3$  mode is responsible for the metal-insulator transition, which explains the drop in conductivity. This result is firmly supported by the group theory analysis that established two primary order parameters:  $X_3$  and  $\Delta_5$ . The monoclinic symmetry  $P2/c$  results from a coupling between the order parameters and simultaneous condensation of both phonon modes.

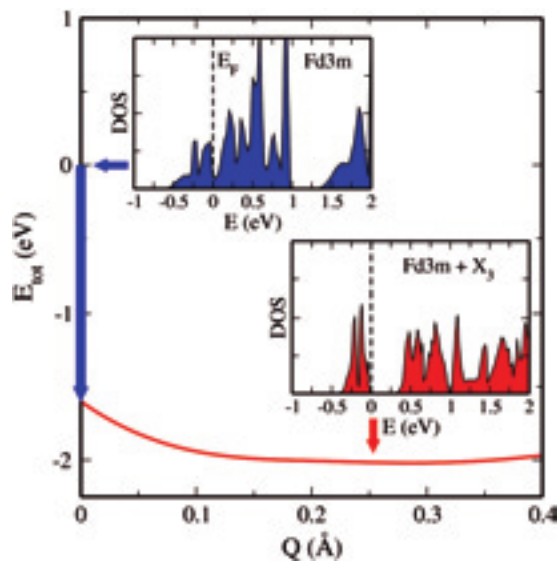


Fig. 1. Total energy as a function of the  $X_3$  phonon amplitude. The blue arrow denotes the energy decrease due to the orbital ordering. The insets present the electron density of states for the metallic (Fd3m) and the insulating (Fd3m+ $X_3$ ) phase

A natural question arises: Why do electron correlations modify electron-phonon interactions *so strongly*? The answer is as follows. In the partially occupied  $3d$  states on iron, the repulsive Hubbard interaction  $U$  reduces electrons' mobility and increases their tendency towards localization. This process activates the orbital degrees of freedom, leading to preferential occupation of  $t_{2g}$  states at the Fermi level. This breaks the symmetry of the wave function and lowers the energy of the system (denoted by the arrow in Fig. 1). Since a new ground state is degenerated in the cubic symmetry, a lattice distortion is necessary to stabilize the long-range order. This happens exactly when the cubic crystal is distorted by the  $X_3$  phonon. It opens the gap by splitting the  $t_{2g}$  states and stabilizes the antiferro-

orbital order with a fractional charge distribution on irons. The existence of similar charge-orbital ordering in the monoclinic phase has been detected by resonant x-ray scattering measurements. Therefore, the phase transition is associated with symmetry breaking in both the electron and lattice subsystems, and the interplay between them is essential for the appearance of the low-temperature insulating phase.

The mechanism we have presented here explains a majority of the experimental facts related to the Verwey transition. It establishes the role of electron interactions and the electron-phonon coupling, connecting the two main concepts of the Verwey transition into one coherent scenario.

## References

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## Activation of dioxygen by zinc alkyls: A new look at an old problem

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Many important biological and industrial processes are based on metal alkylperoxo systems, which are involved in various radical transformations. Alkylperoxo metal intermediates can decompose in

distinct pathways and generate different reactive oxygen species, and the control of these systems presents a continuous challenge for chemists. In this regard, the activation of dioxygen by the main group