



KOÇ UNIVERSITY

Math-Science Seminar

Speaker: Juergen Köhler (Max-Planck-Institut für Festkörperforschung)

Title: Excess Valence Electrons in Novel Low Valent Oxides and Fluorides

Date and Time: Thursday, May 31, 4:45 pm.*

Place: Room Z42, Science Building, Koç University, Rumelifeneri Yolu, Sariyer 80910 Istanbul.

Abstract: The search for new compounds containing low valent metal atoms seems especially worthwhile since unusual chemical and physical properties are mostly connected to the *non-closed*-shell configurations of individual elements. Isolated or condensed metal clusters are found in a great number of reduced transition metal halides and chalcogenides. During the last decades it has become clear that metal cluster formation is also a common feature for transition metal oxides, especially with Mo. It seemed promising to expand this field of chemistry to the neighbouring element Nb, especially as NbO, which has a 'defect rocksalt structure' with 25% ordered vacancies on the anion and cation sites, can be understood in terms of a 'condensate' of Nb₆O₁₂ clusters linked via all apex atoms of the Nb₆ octahedra. Novel reduced oxoniobates with Nb₆O₁₂ clusters, which are condensed via common corners of the Nb₆ octahedra to oligomeric, 1D or 2D infinite cluster units will be presented. Excess valence electrons of the main group elements are often localized in lone pairs, which is especially reflected in the stereochemistry of Ge(II), Sn(II) and Tl(I) fluorides. The investigation of the systems AF₂/MF₄ (A=Ge,Sn; M=Ge,Sn) and TlF/SnF₄ and TlF/TiF₄ has led to the discovery of new complex fluoride-fluorometallates, e.g. [Ge₆F₁₀][GeF₆]. Low valent In fluorides are mainly unknown and all experiments to reduce InF₃ with H₂ or metallic In, failed. Only by complexation with acidic units stable compounds can be obtained, e.g. in InHfF₅ and InBF₄. Band structure calculations show that lone pairs of In⁺ have pure s-character and In⁺ is a very large ion. The reduction of InF₃ with elemental In and Pt powder resulted in a new class of low valent fluorides such as PtIn₇F₁₃, Pt₃In₂₂F₄₀ Pt₂In₁₄Ga₃O₈F₁₅, in which the characteristic building units are [PtIn₆]¹⁰⁺ octahedra exhibiting very short Pt-In distances of 255 pm. These units contain 18 valence electrons and quantum mechanical calculations show, that within the PtIn₆ octahedra both Pt-In interactions and In-In interactions are present. The HOMO of a [PtIn₆]¹⁰⁺ cluster is the t_{1u} state and the calculated band gap Δ₀ is determined by the difference in energy between this state and e_g* (LUMO). This band gap Δ₀ is, as expected, slightly bigger than the optical gap determined by UV absorption spectroscopy of approximately 3.3 eV, which corresponds to the pale yellow colour of the crystals of PtIn₇F₁₃ and Pt₃In₂₂F₄₀. The extension of this field to transition metal In-Oxides has led to a whole series of pentlandite type compounds TIn₆(MO₄)₂, and filled Pentlandite variants TIn₆(MO₄)₂O (T = Pt, Ir; M = Zn, Ga, Ge, In, Fe) which also contain octahedral PtIn₆ cluster units. The partially filled pentlandite variants offer possibilities for tailoring physical properties like band gap and ionic conductivity.

*Refreshments to be served in Science Building, Room Z40 at 4:30 pm.