Molecule-based Conductors and Magnets

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We present in this course the development of molecule-based materials from their birth up to now. We stress on conducting materials, magnetic materials and spin cross-over systems. The fundamental backgrounds as well as the prerequisites needed for obtaining these materials are reported. Examples from the broad literatures are shown to support these notions and also to illustrate the achievements in this field.

For organic conductors, we introduce some important notions, such as mixed valence state, transport properties, band filling, etc….

For molecular magnets, we present some strategies currently used to get magnetic interactions, such as spin non-compensation process, orthogonality of orbitals, Mc Connell mechanisms, high spin molecules, indirect exchange interactions.

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From Molecules to Devices: on Requirements and Consequences of the Necessary Processing Step

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Mastering the processing of molecular materials as thin films or oriented nano-objects on surfaces is detrimental for their integration into devices. The techniques that can be applied to grow such films and/or nanowires can be divided into two categories: "dry processes" using deposition from a gas phase medium or "wet processes" using a reaction in solution. Chemical vapor deposition (CVD) and evaporation under ultra-high vacuum (UHVD) belong to the first category while dip coating (DC) and electrodeposition (ED) belong to the second one. Other processes may be applied: polymeric casting, combined vapor deposition and electrolysis, confined electrocrystallisation, Langmuir-Blodgett, …. Depending both on the process and the forecast application, various types of substrates can be used: alkali halide substrates, metals, silicon wafers, glass or polymer substrates. From the description of these techniques we will sort out the precursor characteristics requirements. Examples will illustrate the choice of process depending on the expected materials and the physicochemical properties of their precursors. Finally, we will see how the precursor nature and the process conditions influence the physical properties of the materials.

Review Articles

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Non-Fermi-Liquid Behavior and Quantum Phase Transition in $Ni_3Al_{1-x}Ga_x$ System

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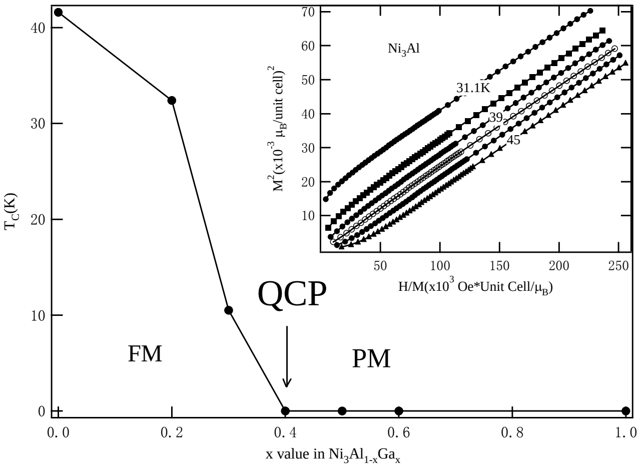
Deviations from Fermi-liquid behavior are a central topic in the experimental and theoretical studies of correlated electronic systems, triggered by the discovery of high T_c superconductivity, and the study of the compounds which can be tuned through zero-temperature phase transitions.

In this lecture, we shall report the results of magnetic susceptibility, resistivity, and specific heat measurements for the $Ni_3Al_{1-x}Ga_x$ alloys. It is found that the ferromagnetic transition temperature T_C decreases with the increasing x value in $Ni_3Al_{1-x}Ga_x$ system. The ferromagnetism disappears in a sample with x value between 0.3 and 0.4, which indicates that there is a zero-temperature phase transition from ferromagnetism to paramagnetism at a critical x_c value, this point in the T-x phase diagram is defined as *Quantum Critical Point (QCP)*. The temperature dependences of susceptibility, resistivity, and specific heat for the samples near *QCP* show the different scaling behaviors from the pure Ni_3Al and Ni_3Ga samples.

The *T-x* phase diagram of $Ni_3Al_{1-x}Ga_x$ alloys is shown in Figure and discussed using the existed theories. We conclude that these different scaling behaviors are due to the spin quantum critical fluctuation near *QCP*. This may be considered as a breakdown of the Fermi-liquid state induced by quantum fluctuation near *QCP*.



The T-x Phase Diagram for $Ni_3Al_{1-x}Ga_x$

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Chemistry and Application of Porous Coordination Polymers

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The recent advent of porous coordination polymers (PCPs), as new functional microporous adsorbents have attracted the attention of chemists due to scientific interest in the creation of unprecedented regular nano-sized spaces and in the finding of novel phenomena, as well as commercial interest in their application for storage, for separation and in heterogeneous catalysis.[1-5] One of the advantages of PCPs, as compared with other microporous materials such as activated carbons, is designability, which provides a variety of surface properties based on organic ligands with functional groups, affording the potential to make the pore surfaces hydrophobic, hydrophilic, chiral and so on. This prominent feature leads us to expect that PCP will show a high adsorption capability for specific molecules. However, few useful concepts and strategies for specific adsorption of smaller molecules have been established to date. Here, we have found superb sorption of C_2H_2 molecules on the functionalized surface of an PCP and show an enhanced "confinement effect", which can be achieved by precisely and regularly arranged functionalities in the nano-sized pore wall, applicable to a highly stable, selective adsorption system.[6] We have succeeded in obtaining interesting array structures of benzene[7] and O_2 [8] molecules and observed their unusual properties in the nanochannel. In addition to these confinement phenomena, we have found that the flexible porous frameworks responding to specific guests are dissimilar to the conventional porous materials. $[Cu(dhbc)_2(4,4'\text{-}bpy)]_n \cdot nH_2O$ is composed of 2D sheet with pi-stack pillars of dhbc, exhibiting dynamic pore contraction without guest.[9] The reversible phase transition occurs by the adsorption/desorption of other supercritical gases such as N_2, CO_2 with about 28% volume change. Two dynamic pillared-layered microporous compounds 1 and 2, $\{[Cd(pzdc)(L)] \cdot xH_2O\}n$ (2:L = 4,4′-azopyridine; x = 2; 3:L = 1,2-bis(4-pyridyl)ethylene); x = 1.5), have nearly the same pore sizes.[10] In case of 1, the micropore expansion occurs after removal of guest while 2 shows pore shrinking on removal of guest.

References

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Susumu KITAGAWA received his Ph. D. from Kyoto University in 1979. He was Professor of Inorganic Chemistry at Tokyo Metropolitan University in the period of 1992 - 1998, and has been Professor of Inorganic Functional Chemistry in Kyoto University since 1998. His main research fields are inorganic chemistry focusing on "Chemistry of Coordination Space," which creates materials utilizing nanovoids, nonlinear phenomena, and quantum effect. He serves as a member of the advisory boards of prominent journals including *Chem. Comm., Chem.Asian J., Chem.Mater. CrystEngComm, Cryst.Growth & Design, Chem.Lett., Inorg.Chim.Acta,* and *Coord.Chem.Rev.*

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Solid State Reaction Mechanisms: Structural Organisation, Charge Ordering and Chemical Reactivity in Non-stoichiometric Solids

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Solid state reactions at ambient temperature play a key role for many technological applications e.g. batteries, membranes in fuel cells or sensors. Our understanding concerning solid state reaction mechanisms is still today quite poor. This naturally limits any optimisation and also the developing and tailoring of new compounds.

In this context the development of oxygen ion conductors working already at room temperatures is of actual interest. For a more general understanding of the diffusion mechanisms, reaction pathways and related activation energies, we have investigated the electrochemical oxygen intercalation into some non-stoichiometric oxides – in particular $(Ca,Sr,Ba)(Fe,Co)O_{2.5+d}$ and $La_2(Co,Ni,Cu)O_{4+d}$ - *in situ* by neutron diffraction and X-ray absorption spectroscopy. Electrochemical oxidation allows to control exactly the oxygen stoichiometry and any structural evolution as a function of the charge transfer. Contrary to classical ion conduction at elevated temperatures - which is generally associated to structural disorder phenomena - ordered intermediate phases have been observed here, showing an extreme complex structural behaviour. Superstructures with unit cell volumes of up to 25000 $Å^3$ have been observed, which implies an exchange of the structural information at distances up to 100 Å. This opens new perspectives not only for the understanding of low temperature diffusion mechanisms in solids but also underlines the general importance of low temperature synthesis and associated long range order in solids.

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He received his Ph. D. degree from the University at Münster, Germany in 1990. After his thesis, he shifted to the Laboratoire Léon Brillouin at the CEA in Saclay, France where he spent one year as a post doc working on high T_c superconductors. In 1991 he became in the same laboratory responsible for the single crystal neutron diffractometer 5C2, installed at the hot source of the ORPHEE reactor. Since 1999 he is Professor of Solid State Chemistry at the University of Rennes. His scientific interests concern the understanding of solid state reaction mechanisms mainly of intercalation compounds and more specifically on solid oxygen ion conductors. For structural investigations he is widely using neutron and synchrotron radiation as well as laboratory X-ray diffractometers.

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