VIII-BB Effects of High Magnetic Field on Chemical and Physical Processes

We have studied the effects of high magnetic field on chemical reaction and physical processes of diamagnetic and paramagnetic materials to unravel the mechanisms of the interaction of matter and magnetic field and to develop unique methods controlling chemical and physical processes and improving chemical and physical properties of functional materials. Currently we are using a vertical superconducting magnet which can generate high magnetic fields (15 T, 1500 T^2/m) in a 40 ϕ bore tube. Magnetic levitation of a water droplet and others is capable using the magnet. It is shown that many chemical reactions and physical processes are significantly affected by the magnetic field. For example, we have succeeded, for the first time, to induce 3D-morphological chirality in zinc silicate membrane tube using a high magnetic field. The results are interpreted in terms of the Lorentz force on ions thermally moving in an aqueous solution. In NaCl:Eu crystals, dislocation mobility is affected by a magnetic field.

VIII-BB-1 3D-Morphological Chirality Induction in Zinc Silicate Membrane Tube Using a Magnetic Field

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We report *three-dimensional morphological* chirality induction using a vertical magnetic field. Right-handed *circular* helix of zinc silicate membrane tube was *selectively* induced by application of a magnetic field (5–15 T), whereas the tube grew straightly upward at zero field as shown in Figure 1. Left-handed circular helix was also selectively obtained by changing experimental condition. *Square* and *triangular* helixes were also prepared. The results are interpreted in terms of the boundary-assisted magnetohydrodynamics mechanism in which cyclotron motion of ions in solution results in one-way convection of the solution near the boundary.

Figure 1. Magnetic field effects on the growth of zinc silicate membrane. (a) 0 T, (b) 6 T, (c) 13.5 T.

VIII-BB-2 Effects of a High Magnetic Field on the Growth of 3-Dimensional Silver Dendrites

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A liquid/solid redox reaction between silver ion and copper metal was investigated under a *vertical* and *inhomogeneous* high magnetic field (maximum field strength: 15 T). 3-Dimensional silver dendrites produced *via* the reaction were affected drastically by the magnetic field. Black and round dendrites were obtained in the magnetic field, whereas metallic silver crystals were grown under the gray dendrites at zero field. The yields of silver dendrite and copper ion increased significantly in the magnetic fields. The results are interpreted in terms of magnetic convection of the solution which is induced by the magnetic force on paramagnetic copper ions generated in the reaction as well as the Lorentz force on ions.

VIII-BB-3 Magnetic Field Effects on TiO_2 Photocatalytic Reaction

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We attempted to examine whether a magnetic field could affect photo-catalytic reaction of titanium oxide, as little was known about the magnetic field effect (MFE) on catalytic reaction. The reaction studied here is as follows,

$$CH_3OH + H_2O + h\nu + TiO_2/Pt \rightarrow 3H_2\uparrow + CO_2\uparrow$$

A methanol-water (1:1) solution containing titanium oxide powder and chloroplatinic (IV) acid hexahydrate was irradiated with light from a xenon lamp in the absence and presence of a magnetic field and the volume of the photo-generated gas was determined. The yield of the gas decreased gradually with increasing a magnetic field from zero to 4 T (*ca.* –10% at 4 T). Similar MFE was observed on the photocurrent of the photo-galvanic cell, $TiO_2(s)|NaOH(aq)||H_2SO_4(aq)|Pt(s)$.

The present MFE is tentatively explained in terms of

a radical pair model (Δg mechanism). Upon photo-excitation of TiO_2, excited singlet TiO_2, $^1TiO_2$*, is generated. While $^1TiO_2$* undergoes intersystem crossing (ISC) to $^3TiO_2$*, singlet electron-hole pair is generated from $^1TiO_2$*. The free electron and hole will be formed by the dissociation of the singlet pair. In a magnetic field, the singlet-to-triplet ISC in the pair is accelerated due to the difference in *g*-values of electron and hole, leading the depression in the yield of free electron and hole by which the succeeding redox reaction is initiated.

VIII-BB-4 On the Movement of Paramagnetic Ions in an Inhomogeneous Magnetic Field

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The movement of transition metal ions was observed in an inhomogeneous magnetic field. The solution containing Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} ions was spotted on a silica gel support, and exposed to magnetic fields up to 410 kOe^2cm^{-1}. The distribution of the metal ions was measured, and the frictional coefficient of the movement was analyzed in relation to the susceptibility and concentration of the metal ions as well as to the size of the silica gel particles. When the concentration is higher, the metal ions move to a larger the distance. It is shown that a large group composed of the metal ions and water molecules moves in a magnetic field.

VIII-BB-5 Magnetic Separation of Metal Ions

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The magnetic separation was investigated for Co^{2+}(9500 × 10^{-6} cm^3mol^{-1}) and Fe^{3+} (14600 × 10^{-6} cm^3mol^{-1}) ions and for Cr^{3+} (6200 × 10^{-6} cm^3mol^{-1}) and Al^{3+} (–2 × 10^{-6} cm^3mol^{-1}) ions. The metal ion solutions were spotted on a silica gel support and exposed to a magnetic field of 410 kOe^2cm^{-1} intensity × gradient. The Co^{2+} ions move to a larger distance toward the maximum field than the Fe^{3+} ions. The result is explained by the fact that the Fe^{2+} ions are adsorbed more strongly on the silica gel support than the Co^{2+} ions. The Cr^{3+} ions move farther toward the field center than the Al^{3+} ions. This occurs because the Cr^{3+} ions are attracted more strongly by the magnetic force than the Al^{3+} ions. It is demonstrated that the separation makes effective use of the adsorption activities as well as the magnetic susceptibilities.

VIII-BB-6 Influence of Magnetic Field up to 15 T on Luminescence of NaCl:Eu Crystals

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Variations of Eu^{2+} luminescent spectra during Eu aggregation in NaCl crystal lattice has been found. These variations caused by extremely high sensitivity of electronic levels splitting to intracrystalline electrical field and Eu^{2+} environment continuously changing during aggregation process. Influence of magnetic field on luminescent excitation spectra in nonequilibrium quenched crystals during the aggregation acted was found (Figure 1). Redistribution of luminescent bands intensity in the excitation spectra gradually increases with the sample exposure in magnetic field (Figure 1). It is unreasonable to suppose that Eu^{2+} ions being paramagnetic can take part in a spin-dependent solid state reaction controlled by magnetic field.

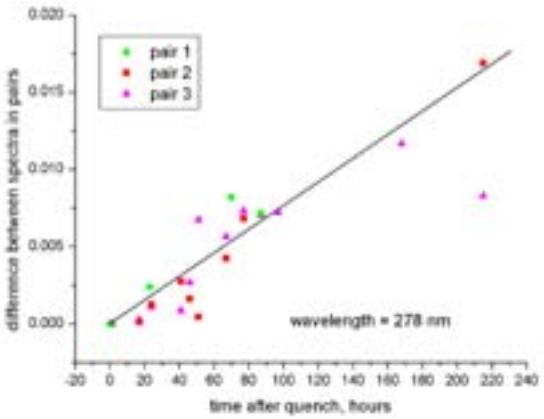

Figure 1. Dependencies of difference between luminescence intensity in reference sample and identical crystal stored in magnetic field after quenching on storage duration for 3 pairs of the identical NaCl:Eu crystals.

VIII-BB-7 Magnetic Field Effect on Dislocation Mobility in NaCl:Eu Crystals

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Recent investigation shown that mobility of dislocations (elementary carriers of plastic deformation) could be considered as an electron spin-dependent process. Magnetic field and its influence on dislocation displacements can serve as a facilities to distinguish spin-dependent part of dislocation interaction with the obstacles. All experiments in this area were carried out early in magnetic fields up to 2 T or in pulsed fields. In this work comparatively strong static magnetic field 15 T was used. It is important because identification of concrete mechanism of spin state mixing in magnetic field as a rule based on correct field dependencies of the magnetic effects.

Displacements of individual dislocation and movement of dislocation in slip bands after exposure of

diamagnetic NaCl:Eu crystals in magnetic field with an induction 15 T were found (Figure 1). Since there was no an external loading of crystals during experiments, the internal stress were the main reason of dislocation displacements. Magnetic field initiates unpinning of dislocations from local obstacles that are Eu aggregates. After magnetic field was switched off increased mobility of the dislocations takes place during 1–2 days. Obtained results open a new possibilities to reliable comparison of theory predictions with the experimental data.

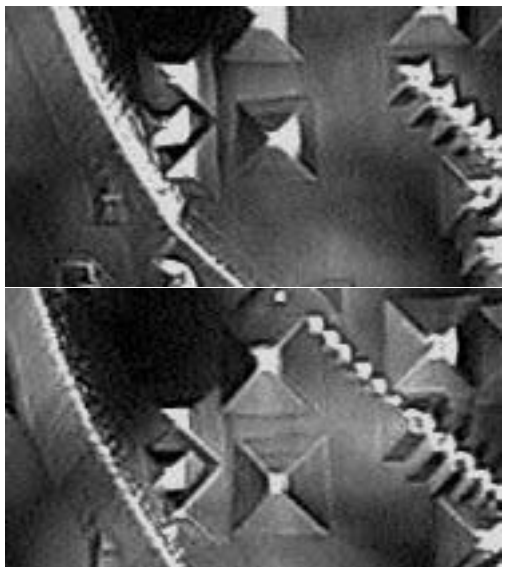

Figure 1. Surface of NaCl crystal a) before, b) after exposure in MF. Big pyramidal pits are initial position of dislocation lines entering on the surface. Small pits are new dislocation line positions after displacement.

VIII-BB-8 Imprinting Magnetic Memory Cells in Molecular Based $NiL_2(C_2H_5OH)_2$ Heterospin Crystals

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Magnetic studies of molecular based crystals have stirred great interest in the magnetic properties of structural defects induced by plastic deformation. In our experiments local deformation of molecular based magnet was carried out by diamond indentor. Local magnetic field around indentation pit was measured by scanning SQUID magnetometer. It has been found that local deformation causes ferromagnetic exchange interaction in $NiL_2(C_2H_5OH)_2$ heterospin single crystals at unusually high temperatures (≥ 77 K). These magnetization temperatures are much higher than the temperature observed for the same, but undeformed crystals (~ 5 K). Ferro- and antiferromagnetic ordering around dislocation cores arise from lattice distortions and changes in distances between the magnetic atoms. Near structural defects high pressure will strongly affect exchange interactions in many spin paramagnetic crystals. Thus, in spite of usual aspiration for perfect crystals grows our experiment shown that disordering can give fruitful results. Local plastic deformation should be considered as a method of control over the magnetic properties of molecular based crystals and as a technique for improving their magnetic characteristics. It offers a nice possibility to imprint the magnetic structure and to distribute magnetic memory cells on the surface premeditatedly. Nanoindentation technologies will probably allow the imprinting of separate magnetic cells ~ 1–10 nm in size.

VIII-BB-9 Localization of Conduction-Band Electrons in β”-(BEDT-TTF)$_4NH_4[Cr(C_2O_4)_3]$·DMF Single Crystals

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Temperature dependence of EPR spectrum of β”-(BEDT-TTF)$_4NH_4[Cr(C_2O_4)_3]$·DMF single crystals, which consists of two separate lines characterizing magnetic features of BEDT-TTF and Cr^{3+} ions, was studied within the range 1.5–300 K. It was found that reconstruction of the EPR spectrum occurs under decrease of the temperature down to $T \approx 20$ K. The reconstruction consists in change of Lorentzian shape of the BEDT-TTF line to Gaussian one and in decrease of the effective magnetic moment of Cr^{3+} ions. Analysis of temperature and orientation dependencies of parameters of the EPR spectra allows one to suppose that localization of conduction electrons within regions with dimensions close to the size of individual BEDT-TTF molecules occurs at $T \approx 20$ K. Exchange interactions between Cr^{3+} ions change towards antiferromagnetic spin correlations as well.

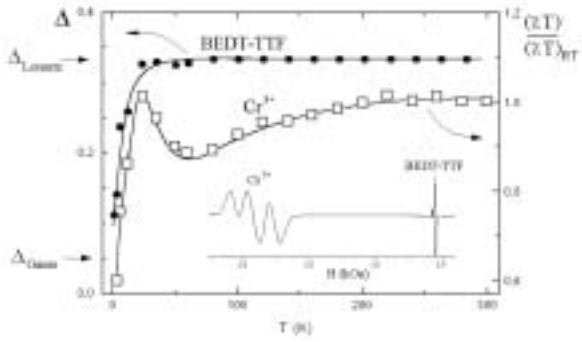

Figure 1. Dependencies of χT and line-shape parameter Δ (Δ = 0.05 for pure Lorenz line and Δ = 0.33 for pure Gauss one) on temperature *T*. ESR spectrum of the salt at room temperature is shown on the insert.