Joint Research Highlights

Quadrupole Orders in Pr-Based Compounds with fcc Lattice Structure

H. Tsunetsugu, T. Ishitobi, and K. Hattori

Recently, physical properties of electric quadrupoles in PrMgNi₄ were studied experimentally and their antiferro ordering has been discussed [1]. Praseodym ions constitute a frustrated structure of fcc lattice, and little had been known for its ordered quadrupolar pattern. Studying this issue theoretically, we have identified various ordered patterns and determined the phase diagram [2].

A non-Kramers doublet is the ground state of Pr³⁺ ion in a crystal field with cubic symmetry, and two components of electric quadrupole are active therein: O₂₀ and O₂₂ with symmetry z^2 and x^2-y^2 , respectively. Despite the same number of degrees of freedom, ordering of those quadrupoles may show different features from those in easyplane magnets due to two reasons. First, while magnetic moments are axial vectors, electric quadrupoles are secondrank tensors, and therefore their effective interactions have a different form. We have determined its minimal form with two parameters J and K corresponding to isotropic and anisotropic couplings. The second reason is the presence of a third order Z₃ anisotropy which time-reversal symmetry prohibits for magnetic moments. This is induced by a hybridization of a singlet excited state, and its excitation energy Δ is another control parameter of this system.

We have employed a mean field approach with a foursite unit and determined the phase diagram at zero and finite temperatures. In the limit of $\Delta \rightarrow \infty$, the Z₃ anisotropy vanishes and three ordered phases appear at low temperatures depending on the ratio of *J* and *K*: O₂₀ ferro, O₂₀ antiferro, and O₂₂ antiferro. For $\Delta < \infty$, the Z₃ anisotropy takes effects and this leads to a phase diagram with rich



Fig. 1. Phase diagram of the *J*-*K*- Δ model for electric quadrupoles on the fcc lattice at temperature $T = 0.1\Delta$. See Ref.2 for details of ordered phases.



Fig. 2. Structure of electric quadrupoles in the zyox phase. Quadrupoles are not ordered on the corner sites.

structure. Related to induced canting of O_{22} components, the most important result is the instability of the two-site antiferro orders to more complex four-site structures. It is also interesting that two of the new phases (zyox and zoxy) exhibit a partial order in which one sublattice remains disordered and quadrupole is polarized as x^2 , y^2 , and z^2 in each of the other three sublattices. They are a triple-q order in which three components with different polarizations and wave vectors are coupled by the Z_3 anisotropy, and we have confirmed their stability by a phenomenological Landau theory. Thus, we have established the basic picture of the phase structure for quadruple orders, and hope that this encourages further experimental studies as well as more advanced theoretical analysis on this issue.

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Authors H. Tsunetsugu, T. Ishitobi^a, and K. Hattori^a ^aTokyo Metropolitan University

Microscopic Theory of the Spin Hall Magnetoresistance

M. Matsuo and T. Kato

Magnetoresistance is one of the fundamental phenomena in the research field of spintronics. Recently, a novel type of magnetoresistance called spin Hall magnetoresistance (SMR) has been observed in a bilayer system composed of a normal metal (NM) and a ferromagnetic insulator (FI) [1]. SMR is explained by the combination of charge-spin conversions in NM and loss of spins at the NM/FI interface [1,2] (see Fig. 1 (a)). When an in-plane charge current is applied to the



Fig. 1. (a) Schematic diagram of the normal-metal(NM)/ferromagneticinsulator(FI) bilayer system for the spin Hall magnetoresistance (SMR) measurement. (b) Experimental data of SMR measured in Pt/NiO/YIG bilayer systems. The data is normalized as -1 at zero temperature using the extrapolated value by the fitting.

NM layer with a large spin-orbit interaction, spin accumulation is caused near the NM/FI interface by the spin Hall effect. The amount of spin accumulation is affected by the orientation of FI magnetization because it changes the rate of spin loss at the interface. A backward spin current owing to spin diffusion is converted into the charge current again by the inverse spin Hall effect and induces longitudinal magnetoresistance, which depends on the orientation of FI magnetization. Recently, SMR has been reported for the bilayer system composed of NM and an antiferromagnetic insulator (AFI) [3], where the orientation of the Néel vector of AFI has been changed by the orientation of magnetization of FI using the NM/AFI/FI trilayer structure.

SMR can be described theoretically by combining the spin diffusion theory with the boundary condition at the interface in terms of the spin-mixing conductance [2]. However, in this theory, the spin-mixing conductance at the interface is a phenomenological parameter that has to be determined experimentally; therefore, its temperature dependence cannot be predicted. Furthermore, the magnetizationorientation dependence of the spin-mixing conductance is assumed phenomenologically by its definition. This semiclassical description of SMR seems to be insufficient for studying quantum features of magnetic insulators such as the effect of thermally excited magnons.

In our work, we constructed a microscopic theory of SMR and derived a general formula of a spin conductance at the interface for both NM/FI and NM/AFI bilayer systems in terms of spin susceptibilities. We clarified that the spin current is composed of static and dynamic parts. The static part of spin current originates from spin flip owing to an effective magnetic field induced by an interfacial exchange coupling. This part is almost independent of the temperature, and takes a maximum when the magnetization (or the Néel vector) is perpendicular to accumulated spins in a normal metal, which is consistent with intuitive discussions in previous experimental studies. However, the dynamic part, which is induced by creation or annihilation of magnons, depends on the temperature, and has opposite magnetization dependence, i.e., takes a maximum when the magnetization (or the Néel vector) is parallel to accumulated spins in a normal metal. The dynamic part becomes larger when the amplitude of the localized spin, S_0 , is smaller. This indicates that the sign of SMR changes at a specific temperature if S_0 is sufficiently small. In Fig. 1 (b), we show the measured temperature dependence of SMR in Pt/NiO/YIG bilayer systems [3]. The sign of SMR changes at 80, 140, and 180 K for NiO thickness of 2.0, 2.2, and 2.7 nm. In addition, we show the fitted curve in the figure using quadratic temperature dependence that is predicted by our theory. This fitting indicates that the quadratic temperature dependence explains well the experimental data at low temperatures. We also derived the Onsager relation between spin conductance and thermal spin-current noise.

This study has been performed as a joint study with Mamoru Matsuo, who was a visiting professor of ISSP in the academic year 2016.

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Authors

T. Kato, Y. Ohnuma^a, and M. Matsuo^a

^aKavli Institute for Theoretical Sciences

Controlling Magnetic Anisotropy of Nano-Size Islands by Alloying

Y. Hasegawa and W. C. Lin

Atomically-thin Fe and Co layers and nano-size island structures formed on the Cu(111) substrate usually exhibit magnetization in the in-plane and out-of-plane directions, respectively. The preferred magnetization directions is due to magnetic anisotropy, and controlling the energy barrier due to the anisotropy are fundamentally important for preserving the magnetization direction and switching it from one of the preferred directions to the other for magnetic storage/ recording and spintronics devices.

The magnetic anisotropy basically originates from the spin-orbit interaction, and in the case of the 3d magnetic elements, the magnetic anisotropic energy (MAE) is described with its perturbation. MAE is, therefore, closely related with the occupation/un-occupation of 3d valence bands near the Fermi energy. In the present study using spin-polarized scanning tunneling microscopy (SP-STM) we investigated how the anisotropy and MAE of the 3d magnetic islands can be controlled by adjusting the valence occupation, that is, by alloying the two elements: Fe and Co, which exhibit the contrasting anisotropic behaviors [1].

Figure 1 shows one of the Co₅₀Fe₅₀ islands pseudomorphically grown on the Cu(111) substrate. The thickness of the triangular island is 2 monolayer, and the white bar in the STM image corresponds to 10 nm. Spin-polarized tunneling conductance spectra taken at the marked site with a Fe-coated W tip exhibits a strong peak at the sample bias voltage of -0.3 V (-0.3 eV below the Fermi level). The peak just below the Fermi level has been assigned to 3d



Fig. 1. Spin-polarized tunneling spectra taken at the marked site of a $Co_{50}Fe_{50}$ island structure presented in the inset STM image. Spectra taken under magnetic fields of 0 T and ±1 T applied in the perpendicular direction to the island are presented. A Fe-coated W tip was used as a spin-polarized probe.

minority states of pure Co and the alloy islands. The peak height varies depending on the magnetic field applied in the perpendicular direction. Since the Fe layer coating the probe tip is in-plane magnetized, the applied magnetic field tilts the probe magnetization toward the field direction. The reduction in the -0.3 V peak height, that is, tunneling from the minority states, by a positive (upward) magnetic field indicates upward magnetization of the alloy island. The magnetic field dependence of the tunneling conductance is also found around -0.5 V. The states there are majority ones as they react to the applied field in the manner opposite to the minority ones.

The magnetic response of the tunneling conductance spectra indicates that the alloy island exhibits perpendicular magnetic anisotropy (PMA). In order to make it clear we swept the applied magnetic field and measured the tunneling conductance at -0.3 V. The obtained result is shown in Fig. 2. Gradual increase (decrease) with the increment (decrement) of the magnetic field is due to the tilt of the probe magnetization by the applied field. Then sudden drops observed around ± 0.12 T are due to the flip of the magnetization of the alloyed island from anti-parallel to parallel directions to the applied field. From the positions the drops, we can measure switching magnetic field or coercivity, which are closely related with the energy barrier between the two PMA configurations.

The PMA energy depends on the size of the islands; basically proportional to the area or the number of the composing atoms. We measured the switching field on



Fig. 2. Tunneling conductance at the sample bias voltage of -0.3 V taken at the center of the CoFe alloy island presented in the right STM image during a sweep of the applied perpendicular magnetic field. The sweeping directions are marked with red dashed arrows. Sudden drops of the tunneling conductance indicate switching of magnetization of the island.



Fig. 3. Plot of switching magnetic field as a function of the number of the constituent atoms for both pure Co and CoFe islands. Coercivity (right vertical axis) was estimated from the switching fields taken with an antiferromagnetic tip, whose stray field is negligible.

various sizes of the alloy islands, and the results are summarized in Fig. 3 and compared with those taken on pure Co islands. One can clearly find that the switching field of the alloy islands is significantly reduced from pure Co islands by a factor of 3-4. For both Co and CoFe alloy islands, the switching field gradually increases with the size of the islands or the number of the composing atoms, but around 8000 atoms it exhibits saturation or even reduction with the island size. The peculiar behavior of the switching field is explained with a crossover of two magnetization reverse processes; for small islands the magnetization flips at a time whereas large islands are reversed through a process of domain wall nucleation and propagation. It should be noted here that since a ferromagnetic tip is used stray field from the tip significantly reduces the switching field; through the comparison with the switching filed measured with an antiferromagnetic Co-coated tip, which directly provides coercivity, we estimated coercivity of our samples as depicted in the right axis of Fig. 3. Nevertheless, the results presented in Fig. 3 clearly indicate that the switching field is significantly reduced by the alloying, and suggest that the crossover same as pure Co islands also occur on the alloy islands.

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Authors

H.-H. Yang, C.-C. Hsu^a, W.-C. Lin^a, and Y. Hasegawa ^aNational Taiwan Normal University

Free-Standing Oxide Thin Film Membranes

R. Takahashi and M. Lippmaa

A fundamental parameter that determines the physical properties of crystalline materials is the lattice parameter, which is generally determined by the chemical composition and the lattice type of a crystal. Options for tuning materials properties or electronic phases by changing the lattice parameters is generally limited to the use of thermal expansion, the application of mechanical pressure, or ionic substitutions - also known as chemical pressure. Thin films offer an additional option of using epitaxial strain for lattice parameter control, since nanometer-scale films grown on singlecrystal substrates tend to assume the same in-plane lattice parameter as the substrate material. Even in mechanically hard materials, such as oxides, epitaxial tensile or compressive strains of several percent can be routinely obtained. Larger strain states, however, are difficult to obtain without mechanical failure of a crystal. Likewise, it can be difficult to fabricate entirely strain free thin films. An interesting technique that can be used to apply very high local or longrange strain fields on thin layers is the use of free-standing thin films. In our recent work, we have developed a new oxide thin film lift-off process based on the use of latticematched BaO sacrificial layers to grow thin films that can be released from a substrate and transferred to a secondary carrier [1]. The technique can be used to extend the achievable range of mechanical strain in oxide materials and is the basis for constructing novel vibrational energy harvesting devices.

The process of fabricating free-standing BaTiO₃ films is illustrated in Fig. 1. A sacrificial BaO layer is first grown on a SrTiO₃ substrate. The BaO layer is nearly lattice matched with titanate lattices and can be grown epitaxially on the substrate surface. The membrane material, in this case BaTiO₃, is grown on top of the sacrificial BaO layer. The heterostructure is then removed from the thin film growth chamber and attached with an adhesive layer to a flexible secondary carrier, such as a glass sheet or even a polymer backing. When the whole structure is immersed in water, the BaO layer dissolves, detaching the single-crystal substrate from the membrane layer, as illustrated in Fig. 1c, which shows the detached membrane on a secondary flexible carrier and the detached substrate. In principle, the substrate can be recycled for growing another thin film.

One interesting application of the membrane process is the development of piezoelectric energy converters for harvesting vibrational energy. The use of a membrane device is benefitial because the piezoelectric film, such as BaTiO₃, can be grown epitaxially under optimal growth conditions on a high-quality single crystal substrate, yielding the highest piezoelectric coefficient. However, the bulk substrate prevents the application of large strains on the film, as is required for low-frequency vibrational energy harvesting. Much higher strains can be achieved in a membrane device where the piezoelectric film is detached from the substrate and sandwiched between flexible conducting electrodes,



Fig. 1. Free-standing oxide thin film membrane fabrication process: (a) growth of a sacrificial BaO layer and the functional membrane layer, (b) attaching the heterostructure with a poly-dimethylpolysiloxane (PDMS) adhesion layer to a indium tin oxide-coated polyethylene terephthalate (PET) carrier, and (c) removing the substrate by dissolving the BaO layer in water.



Fig. 2. Construction of a vibrational energy harvesting device consisting of a $BaTiO_3$ membrane embedded between two ITO/PET electrodes (a). The actual test device is shown in the inset of (b). The voltage signal obtained by vibrating the test device at 5 Hz is shown in (b).

as illustrated in Fig. 2a. An energy harvester device can be constructed by supported a flexible membrane cantilever from one end and attaching a test mass on the free end. When mechanical vibration is applied, a periodic current can be generated in an external circuit, powering, for example, a low-power environmental sensor device. The output signal of a test cantilever using a BaTiO₃ film is shown in Fig.2b.

The demonstration of the process used a BaTiO₃ film, but the technique itself is applicable to any material that can be grown epitaxially on the sacrificial BaO layer. For energy harvesting devices, a flexible backing is generally required to maintain the integrity of a millimeter-scale membrane.

An obvious use of the technique is to fabricate films that are truly strain free and for this reason, the technique has much broader potential applications than flexible piezoelectric energy conversion devices.

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Authors R. Takahashi^a, and M. Lippmaa ^aNihon University

Lasing Dynamics in Perovskite Microcavities

S. Chen and H. Akiyama

Perovskite materials have shown remarkable progress in both the field of solar cell and light emitting devices, for solar cell, conversion efficiencies more than 25% have been achieved, and for light emitting devices, perovskitebased vertical cavity surface emitting lasers (VCSEL) and distributed feedback (DFB) lasers have been fabricated, and very fascinating single-mode lasing properties have been demonstrated, however, the detailed lasing mechanism is still unclear. We have fabricated various kinds of CePbBr₃ perovskite microcavities with a low-temperature liquid-phase growth method, such as microplate, microrods, and microcubes, as shown in Figure 1, with a size from several tens to 200 micrometers. A clear substrate dependence of the morphologies of the perovskite microstructures in this growth method has been observed [1]. With the excitation of a femtosecond laser beam from a Ti: sapphire ultrafast laser system, all the microcavities show lasing behavior under elevated excitation densities, the higher carrier density more that Mott density at lasing threshold indicates the lasing behavior in these perovskite microcavities should be mainly related to electron-hole plasma rather exciton.

The lasing dynamics of the microcavities were further studied with time-resolved photoluminescence system. Figure 2 shows the spectrally and temporally resolved lasing images recorded by a streak camera. With increasing excitation fluences, two importance features have been observed, one is the redshift of the dominant lasing spectra to the low energy side due to the band gap renormalization (BGR) effect, another one is the blueshift of each lasing mode to higher energy side due to the reduction of the refractive index caused by the high injection carrier density. At a certain excitation density, for example 180 μ J/cm², we can see a redshift of each mode to low energy side with time going on after excitation, which indicates a recovery of index in microcavity, and the blueshift of the total lasing spectra with time going on indicates a recovery of BGR, therefore the lasing dynamics is merged with the transient BGR effect and the transient change of refractive index in perovskite microcavities, detailed explanations can be found in the published paper [2].

We also fabricated CsPbBr₃ perovskite nanocrystals with a ligand-assisted recrystallization method, and sandwiched the perovskite nanocrystals with two high-reflectivity distributed Bragg reflectors (DBRs) to form a VCSEL device [3]. The lasing performances of the perovskite nanocrystal



Fig. 1. SEM micrograph of CsPbBr₃ single-crystal microcavities on substrates of (a) single-crystal Si, (b) sapphire, and (c) amorphous quartz. Streak-camera images (d) of the emissions from microplate with various excitation densities. In the vertical dimension, a time range of 40 ps for each slice is shown. The distinct lasing modes are labeled as Mode A (with the highest photon energy) to Mode G (with the lowest photon energy) above the threshold. In each slice, a redshift to low energy with time for each mode is clearly demonstrated. Inset is a lasing image of a microplate under the excitation of femtosecond lasing beam, showing a whispering-gallery mode (WGM) lasing.



Fig. 2. (a) TEM image of CsPbBr₃ perovskite nanocrystals with an average size around 12 nm, (b) Schematic of the CsPbBr₃ nanocrystal based VCSEL, where the CsPbBr₃ nanocrystals are sandwiched with two high-reflectivity DBRs. (c) Emission spectra of the VCSEL with different excitation densities. The inset shows a waveform of the output pulse with a pulse width of 23 ps from the VCSEL with an excitation density 2 times of the threshold.

based VCSEL have been characterized with femtosecond pulse excitations, and single-mode lasing of the VCSEL has been observed. The threshold excitation density was around 8 μ J/cm². The cavity quality factor Q of the VCSEL is estimated to be around 1425. With the excitation power over 2 times of the threshold, the output pulse width of the perovskite based VCSEL is measured to be around 23 ps, demonstrating a potential application in short pulse generation of perovskite based VCSELs. Investigations on the carrier dynamics in the VCSEL is still in progress.

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Authors

S. Chen^a and H. Akiyama ^aEast China Normal University

Second Hydrogen-Ordered Phase of Ice VI: Ice XIX

R. Yamane, K. Komatsu, and Y. Uwatoko

Ice exhibits extraordinary structural variety in its polymorphic structures. To date, more than 20 crystalline and amorphous phases of ice have been reported.

The existence of a new form of diversity in ice polymorphism has recently been debated in both experimental and theoretical studies, questioning whether hydrogen-disordered ice can transform into multiple hydrogen-ordered phases, contrary to the known one-to-one correspondence between disordered ice and its ordered phase. Recent experiments on a high-pressure hydrogen-disordered phase, ice VI, revealed an unknown hydrogen-ordered form besides the known ordered phase, ice XV. However, due to experimental difficulties under the high-pressure condition, the intriguing manner of hydrogen ordering in ice VI has been investigated only using decompressed sample to ambient pressure. Also,



Fig. 1. Representative experimental paths of dielectric and neutron diffraction experiments described in the phase diagram of ice obtained herein. Phase boundaries among ice VI, ice XV, and ice XIX are described by black solid lines, based on dielectric experiments (red and blue squares correspond to phase transition temperatures from ice VI to ice XV and XIX, respectively). The dotted line shows the provisional phase boundary between ice XV and ice XIX.

no previous study reports direct experimental evidence for the multiplicity of hydrogen-ordered phase of ice VI. We report a second hydrogen-ordered phase for ice VI, ice XIX, unambiguously demonstrated by in-situ dielectric and neutron diffraction measurements under high pressure originally developed by our group [1]. Based on a newly obtained phase diagram of ice VI, XV and XIX (Fig. 1), we revealed that ice XIX is thermodynamically stabilized by pressure compared to ice XV.

To investigate hydrogen ordering of ice VI in its stable pressure region, comprehensive dielectric experiments were first carried out in the pressure range 0.88–2.2 GPa, using a newly developed pressure cell. Ice VI was initially obtained at room temperature and its dielectric properties were determined in both cooling and heating runs in the temperature range 100–150 K. Neutron diffraction experiments were conducted at 1.6 and 2.2 GPa, in which ice XIX appears as hydrogen-ordered phase of ice VI based on the dielectric experiments, using Mito-system at J-PARC [2]. Both cooling and heating runs were conducted at each pressure in the temperature range 80–150 K.



Fig. 2. a Dielectric constant and dielectric loss of HCI-doped ice VI and its hydrogen-ordered phase (ice XIX) obtained at 1.9 GPa upon cooling. b Neutron diffraction patterns of ice VI and XIX obtained at 1.6 GPa in the cooling run. Only an expanded area showing new peaks of ice XIX is displayed. The blue and black ticks represent all the peak positions expected from the unit cells of ice XIX and ice XV, respectively. Blue triangles indicate new peaks at 2.20 Å and 2.26 Å, which do not appear from the unit cell of ice XV.



Fig. 3. Proposed crystal structure of ice XIX based on Pcc2 structure model.

Phase transitions from ice VI to its hydrogen-ordered phases were observed at around 120–130 K, along with sudden weakening of the dielectric response of ice VI with decreasing temperature (Fig. 2a). The reason for this weakening is that hydrogen ordering of ice suppresses reorientation of water molecules which induces the dielectric response of ice. The transition from ice VI to ice XIX was also observed in the neutron diffraction experiments, as appearance of new peaks due to symmetry lowering (Fig. 2b). Some of the new peaks, e.g. those at 2.20 Å and 2.26 Å (indicated by blue triangles in Fig. 2b), cannot be explained by the structure of ice XV. This is unambiguous evidence that ice VI has a hydrogen-ordered phase distinct from ice XV, and we named this unknown phase as ice XIX.

Based on the phase boundary of ice VI and its hydrogenordered phases, ice VI contracts upon hydrogen ordering, which thermodynamically stabilizes ice XIX in the higherpressure region compared to ice XV because of its smaller volume than ice XV.

In addition, from our structural analysis, two structural models, whose space groups are $P\overline{4}$ and Pcc2, are the most plausible for the crystal structure of ice XIX (the Pcc2 structural model is shown in Fig. 3). It should be noted that the proposed structure models intrinsically include hydrogen atoms whose site occupancy is 50 %; in other words, the models exhibit that ice XIX is partially ordered state. This indicate a possibility that there exists another fully hydrogen-ordered phase of ice VI instead of the partially hydrogen-ordered ice XIX considering the third law of thermodynamics. Considering the suggested space group of ice XV, P1 or Pmmn, centrosymmetry of hydrogen configurations is the most significance difference in hydrogen configuration between ice XIX and ice XV. Such symmetry difference would induce intriguing difference of physical properties between ice XIX and XV in terms of such as optic and dielectric.

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R. Yamane^a, K. Komatsu^b, J. Gouchi, Y. Uwatoko, S. Machida^c, T. Hattori^d, H. Ito^b, and H. Kagi^b ^aTohoku University

^bThe University of Tokyo

Neutron Science and Technology Center, CROSS

dJ-PARC Center, Japan Atomic Energy Agency

Fabrication of a Compact Cubic-Anvil Pressure cell

N. Fujiwara and Y. Uwatoko

We have succeeded in fabricating the smallest cubic-anvil pressure cell (CAPC) to date. This miniaturization allowed us to investigate physical properties at high pressures of over 4 GPa under a magnetic field [1, 2].

In strongly correlated electron systems, one of the most intriguing topics is the quantum phase transition. Unlike a conventional thermally induced phase transition, this phase transition is driven via quantum fluctuations at zero temperature, leading to an unconventional ground state even at finite temperatures. Pressure is a representative parameter as well as carrier doping in this phase transition. At low pressures below 3-4 GPa, a piston-cylinder pressure cell (PCPC) has been most widely used for various experiments because of its large sample space. However, this pressure cell is unavailable at high pressures above 4 GPa. The CAPC marks high hydrostaticity among pressure cells available at pressures above 4 GPa. Conventionally, the CAPC has not been suitable for measurements that require a magnetic field due to its large body size. In fact, the CPAC has been used mainly for resistivity or alternating-current susceptibility and recently for neutron-scattering measurements at zero field [3].

We have fabricated the smallest PCAC to date using $\phi 60$ NiCrAl guide blocks and investigated pressure homogeneity from ⁶³Cu nuclear-quadrupole-resonance (NQR) linewidth of Cu₂O. The NQR frequency is proportional to the electric field gradient at a ⁶³Cu site and the spectral shape is sensitive to local disorder or inhomogeneity. Therefore, the NQR measurements are available for investigating hydrostaticity inside the pressure cell.

Figure 1(a) shows a sectional view of the CAPC, and Fig. 1(b) shows a bird's-eye view of three WC anvils mounted on the $\phi 60$ NiCrAl guide block. The four WC anvils are fitted in the NiCrAl sliding blocks covered with Teflon sheets. The four anvils move toward the 6.0-mm pyrophyllite cube without friction when the load is imposed on the NiCrAl guide blocks. The cube is made of lower and upper pyrophyllite gaskets and contains a $\phi 3.0$ Teflon capsule (see the inset of Fig. 2(a)). A single coil wound around Cu₂O power samples is inserted into the Teflon capsule filled



Fig. 2. (a) Bird's-eye view of a ϕ 3.0 Teflon capsule mounted on a pyrophyllite gasket. A nuclear-quadrupole-resonance (NQR) coil wrapped around powder samples of Cu₂O is inserted into the capsule. The inset shows upper and lower gaskets and a Teflon capsule. (b) Overview of the ϕ 3.0 Teflon capsule on the gasket. The inset shows the ϕ 2.0 Teflon capsule used for the resistivity measurements.

with pressure transmitting media, the mixture of fluorinate FC-70 and FC-77 (see Fig. 2(a)). An overview of the ϕ 3.0 Teflon capsule on the gasket is shown in Fig. 2(b). The Teflon capsule has a ϕ 2.5 × 1.5 mm sample space and is significantly larger than that used for conventional resistivity measurements (see the inset of Fig. 2(b)).

Figure 3(a) shows the 63 Cu-NQR spectra of Cu₂O measured at room temperature with a conventional spectrometer and the $\phi 60$ CAPC. The spectra were obtained using the fast Fourier transform of the spin-echo signal. Figure 3(b) shows the pressure dependence of the NQR linewidth. The linewidth for the CAPC is compared with that for the PCPC. The NQR spectra for the PCPC exhibited double-peaks structure above 2 GPa [1], and the data below 2 GPa were plotted in Fig. 3(b). The linewidth for the PCPC increases with increasing pressure above 0.8 GPa where the mixture of the FC-70 and FC-77 begins to freeze, whereas that for the CAPC saturates at high pressures above 4 GPa. The pressure homogeneity for the CAPC is better than that for the PCPC in a high-pressure regime. This result suggests that pressure application from multiple directions suppress the inhomogeneity much more effectively than uniaxial pressure application.

In conclusion, we have fabricated a CAPC having a diameter of 60 mm, the smallest cubic-anvil cell to date, which allowed us to measure physical properties under a magnetic field utilizing a superconducting magnet with a large-bore sample space greater than 100 mm. In this pressure cell, a large sample space having $\phi 2.5 \times 1.5$ mm was secured. This pressure cell would open a new avenue for the quest for novel pressure-induced phenomena in strongly correlated systems.



Fig. 1. (a) Sectional view of a cubic anvil pressure cell (CAPC) with ϕ 60 NiCrAl guide blocks. (b) A bird's-eye view of three WC anvils and a pyrophyllite cube mounted on the lower NiCrAl guide block.



Fig. 3. (a) 63 Cu-NQR spectra of Cu₂O measured with the CAPC at room temperature. (b) Half width at half maximum of the NQR spectra measured using the CAPC (black open circles) and NiCrAl piston-cylinder pressure cell (blue open circles). The curve is a guide for the eye.

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Authors N. Fujiwara^a and Y. Uwatoko ^aKyoto University

Magnetoelectric Effect in the Antiferromagnetic Ordered State of Ce₃TiBi₅ with Ce zig-zag Chains

M. Shinozaki, G. Motoyama, and Y. Uwatoko

Some magnetoelectric effects, including the Edelstein effect, often occur in the materials without some inversion symmetry. Materials exhibiting such cross-correlation are expected as various new functional materials. Recently, a new magnetoelectric effect is attracting attention in the metallic antiferromagnetic compound, in which the spatial inversion symmetry is broken at the magnetic site. This new cross-correlation is understood as a phenomenon that appears as a result of the realization of odd parity multipole [1, 2].

We discovered a new antiferromagnetic heavy fermion compound Ce₃TiBi₅ in which the local inversion symmetry at cerium site is broken (Figs. 1(a) and (b)). The crystal structure of Ce₃TiBi₅ is $P6_3/mcm$, and the global inversion symmetry is maintained. Therefore, the current-induced magnetization phenomenon in the sense of the Edelstein effect does not occur. Ce₃TiBi₅ has only one cerium site, and the cerium forms zigzag chains along the *c*-axis. The antiferromagnetic ordering temperature of T_N is 5.0 K, electrical resistivity, magnetic susceptibility, and specific heat show a distinct anomaly, respectively. Some odd parity multipoles are expected in the antiferromagnetic state, although the magnetic structure has not yet been determined (Fig. 1(c)).

We performed the magnetization measurements with applying several constant electric currents parallel to the *c*-axis of Ce₃TiBi₅ at around $T_{\rm N}$ using commercial magnetometer of MPMS. In this measurement, slight static magnetic field was applied to determine the sample position. Current-induced magnetization ($M_{\rm ME}$) was obtained from subtracting magnetization induced by applying slight static magnetic field and zero electric current as blank magnetization.

We have succeeded in measuring the current-induced magnetization only on the antiferromagnetic state [3, 4]. Figure 2(a) shows the temperature (*T*) dependence of M_{ME} on Ce₃TiBi₅. It is found that $M_{\text{ME}}(T)$ starts to appear just below T_{N} with decreasing *T*, although it is almost independent of temperature and is approximately zero above T_{N} . This *T* dependence was also observed at several electrical current (*i*), and then we show plots of M_{ME} versus *i* at 3.0 K in Fig. 2(b) to discuss the *i* dependence of the magnitude of M_{ME} . M_{ME} shows the linear *i* dependence, which suggests that M_{ME} on Ce₃TiBi₅ linearly increases with an increase in the electric field.

Next, *T* dependence of M_{ME} at several magnetic field (*H*) is shown in Fig. 2(c). $M_{\text{ME}}(T)$ exhibits an identical curve despite a difference in the magnitude of *H*. The magnitude of M_{ME} at each magnetic field and T = 3.0 K was decided from the $M_{\text{ME}}(T)$ at several magnetic fields ($5 \le H \le 40$ Oe) and is plotted in Fig. 2(d). The magnitude of M_{ME} is independent of *H* in this field range, which indicates that M_{ME} has a similar value even in zero magnetic field.

The current-induced magnetization was observed only below the antiferromagnetic transition temperature of 5.0 K. This current-induced magnetization exhibits linear dependence with respect to the DC electric current and demonstrates little dependence on the magnetic field, i.e., the behavior persists even in zero magnetic field. Based on these



Fig. 1. (a) Top view of the crystal structure of Ce₃TiBi₅. (b) Schematic side view of the crystal structure, where only Ce ions on a front side are drawn for clarity. Green line denotes a unit cell. Black circles indicate the position of the inversion center. (c) Magnetic structure on the Ce-zigzag chain, where the unit cell does not change even at the ordered state. Orange arrows on the Ce ions indicate the expected ordered magnetic moments below $T_{\rm N}$. The red mark denotes a toroidal moment on a Ce ion at the ordered state, which is a candidate as a realized odd multipole state on Ce₃TiBi₅.



Fig. 2. (a) Comparison of the *T* dependence of the M_{ME} between several *i* for sample A. (b) *i* dependences of M_{ME} at 3 K for samples A and B. (c) Comparison of the *T* dependence of M_{ME} between different *H*. (d) *H* dependence of M_{ME} at 3 K.

results, we suggest that the current-induced magnetization originated from the magnetoelectric effect of the odd multipole state on the Ce-zigzag chain structure. Meanwhile, the sign and magnitude of the slope of *i* dependence of $M_{\rm ME}$ has large sample dependence as shown in Fig. 2(b). We consider the sample dependence to be explained by the imbalance of the domain structure of the AFM state. However, we do not know what kind of domain structure is realized in the antiferromagnetic state. We are conducting experiments with an interest in the consistency between the realized odd parity multipole state on Ce3TiBi5 and the current-induced magnetization measurements with various geometry.

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Authors

M. Shinozaki^a, G. Motoyama^a, J. Gouchi, S. Nishigori^a, T. Mutou^a, A. Yamaguchi^b, K. Fujiwara^a, K. Miyoshi^a, and Y. Uwatoko ^aShimane University

^bUniversity of Hyogo

High Precision Study of the Anderson Transition

T. Ohtsuki and K. Slevin

More than six decades have passed since Anderson's seminal paper on localization. During the subsequent decades, there have been numerous important discoveries including weak localization, universal conductance fluctuations, and the scaling theory of localization. Since the proposal of the scaling theory, determining the critical behavior of the localization-delocalization transition, which is usually referred to as the Anderson transition (AT), has continued to attract considerable attention.

One of the most widely used approaches to study the AT quantitatively is to calculate the Lyapunov exponents (LE's) and to analyze them using finite size scaling. Large scale computations using the supercomputer System B at ISSP have enabled us to calculate LE's with high precisions for very large system sizes. We consider a system of size $L_x \times L \times L$, which we divide into layers of an $L \times L$ square. The transfer matrix M relates the wave functions on the 1st layer to L_x th layer, and the LE's are the eigenvalues of the matrix $\Omega = \lim_{L \to \infty} \ln (M^{\dagger}M)/2L_x$. From the smallest positive LE, γ , we define a quantity $\Gamma = \gamma L$.

The conventional method requires the simulation of a single very long sample. While this method has been employed very successfully in numerous simulations over the preceding decades [1], the calculations are inherently serial and do not allow us to take advantage of massively parallel computing. We devised an alternative method to simulate an ensemble of much shorter samples and take an ensemble average, allowing us to make full use of System B.

We have analyzed the LE's using finite size scaling, and estimated the critical exponent for the divergence of the correlation length, v = 1.572 [1.566,1.577] for three dimensional (3D) Anderson model of localization [1,2],



Fig. 1. Γ as a function of the disorder strength W in the 3D Anderson model of localization for various cross section size L = 12.18, 24, 32,48 and 64. L = 96 is underway using new System B.

 $H = \sum_{i} \varepsilon_{i} |i\rangle \langle i| - \sum_{\langle i,j \rangle} |i\rangle \langle j|$, where ε_{i} is the onsite random potential distributed uniformly in [-W/2, W/2]. We fit the W and L dependence of Γ using finite size scaling (Fig. 1).

The critical exponent changes when a magnetic field is applied. This can be realized by inserting Peierls phase in the nearest neighbor transfer. We obtain v = 1.443 [1.437,1.449] which is distinctly different from the case without a magnetic field [3].

At the critical point, the wave functions exhibit multifractality, hence the local density of states fluctuates significantly. If we consider dilute magnetic impurities, the Kondo temperature $T_{\rm K}$ varies from one magnetic impurity to another due to the large fluctuations of wave functions (Fig. 2). We have calculated the local density of states at the critical point using the kernel polynomial method and calculated the Kondo temperature distribution [4]. The massively parallel calculations on System B enabled us to reach the small $T_{\rm K}$ needed to check the analytic prediction.

In addition to the cases of Anderson's model of localization with and without magnetic fields, depending on whether we have spin-rotation symmetry, chiral symmetry as well as particle-hole symmetry, we have 10 symmetry classes for random quantum systems. In recent years, the non-Hermitian systems with randomness, which are classified into 38 symmetry classes, are attracting renewed interests. We have studied the critical behaviors of AT with chiral



Fig. 2. Schematic of a magnetic impurity and a multifractal wave function.

and/or particle-hole symmetries [5], and most of the critical exponents for the AT in 3D are now determined. In addition, we have verified that the transfer matrix method and the finite size scaling work for non-Hermitian systems. We are now studying the localization-delocalization transition for non-Hermitian systems [6,7] and determining the critical exponents, which might explain the critical behavior of light localization.

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Authors

T. Ohtsuki^a and K. Slevin^b ^aSophia University ^bOsaka University

Spin Waves in the Two-Dimensional Honeycomb Lattice XXZ-Type van der Waals Antiferromagnet CoPS₃

C. Kim, J. G. Park and T. Masuda

The recent introduction of magnetic van der Waals (vdW) materials has opened new and novel opportunities to examine the low-dimensional magnetism in real materials. In particular, $TMPS_3$ (TM = Mn, Fe, Co, Ni) family has attracted special interests in the community as a class of antiferromagnetic 2D vdW materials. The crystal structure of $TMPS_3$ is a monoclinic structure with a C 2/m space group, where a weak vdW force couples honeycomb layers with edge-shared TMS_6 octahedra on the *ab*-plane along the *c*-axis. Since magnetic structure and exchange interactions in $TMPS_3$ depend on the TM elements, they provide an excellent playground to validate spin dynamics theory in low dimensions experimentally.

CoPS₃ has been less studied among them due to the difficulty in synthesizing high-purity samples [1]. Therefore, the magnetic Hamiltonian of CoPS₃ has been unknown so far and needs investigation. CoPS₃ has antiferromagnetic phase transition at $T_N = 122$ K with zig-zag magnetic order. The spins are aligned along the *a* axis with a small canting to the *c* axis. The magnetic susceptibility shows a difference between H // ab and H // c in the paramagnetic state, which implies XY-like anisotropy [1].

Moreover, Co^{2+} magnetic systems have recently drawn significant attention because Co compounds may host Kitaev interactions [2]. A spin-orbital entangled state is an essential ingredient to realize the Kitaev interactions, which can be verified by measuring spin excitations. Typically, a spin-orbit exciton, the crystal field excitation between $J_{eff} = 1/2$ to 3/2 state, is strong evidence of a spin-orbital entangled state. Most cobalt compounds have such excitation at 20~30meV, proportional to the strength of spin-orbit coupling of cobalt [3].

In this study [4], we examined such a possibility using inelastic neutron scattering at the time-of-flight spectrometer of HRC at J-PARC. Our temperature-dependent measurements show that CoPS₃ does not show the spin-orbit exciton expected near 30 meV at high temperature in stark contrast with initial expectations. Figure 1 shows the temperature dependence of magnetic excitations. Above $T_{\rm N} = 122$ K, there is no sign of excitations near 30 meV. This can only be interpreted as evidence for the ground state of CoPS₃ being an S = 3/2 state, not the spin-orbital entangled $J_{eff} = 1/2$ state. Figure 2 shows the spin-wave spectrum of CoPS3 with incident neutron energy $E_i = 71$ meV. The measured spin-wave spectrum shows two magnon branches over 40 meV with a massive 13 meV spin gap. Also, the spin-wave spectrum shows extra gap-like features at 24~27 meV. Based on the former analysis about temperature dependence of magnetic excitations, we use magnetic Hamiltonian with S = 3/2 system to explain the spin-waves of CoPS₃. This magnon was wellfitted using an anisotropic Heisenberg (XXZ) model with a reasonable anisotropy coefficient $\alpha \equiv J_z/J_x = 0.6$ and strong easy-axis single-ion anisotropy K = 2.4 meV along the a







Fig. 2. The experimental INS data of CoPS₃ measured at T = 8 K with $E_i = 71.3$ meV is shown in (b). (a), (c) The best-fit magnon spectra with the XXZ model and the isotropic Heisenberg model. An instrumental energy resolution of 3 meV was used to convolute the theoretical results shown in (a) and (c). Horizontal and vertical white boxes denote the integration range for the constant-*E* and constant-*Q* cuts in (d-g), respectively. (d), (e) Constant-*Q* cut at the momentum range of $Q = [1.7 \ 1.8]$ and $Q = [2.2 \ 2.3]$ Å-1 for the measured data with the best-fit simulations. (f), (g) Constant-*E* cut with the energy range of $E = [13 \ 16]$ and $E = [24 \ 27]$ meV

axis. The magnetic structure from our magnetic Hamiltonian also consistent with the reported magnetic structure. In summary, our experiment and theoretical analysis suggest CoPS₃ as another exciting platform to study anisotropic XXZ-type spin Hamiltonian in the honeycomb antiferromagnet. Moreover, it provides an excellent playground for future investigation of low-dimensional magnetism with magnetic van der Waals materials.

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Authors

C. Kim^a, J. Jeong^a, P. Park^a, T. Masuda, S. Asai, S. Itoh^b, H. S. Kim^c, A. Wildes^d, and J. G. Park^a ^aSeoul National University ^bKEK ^cKangwon National University ^dInstitut Laue-Langevin

Quantum Spin Liquid State in a Square-Kagome Antiferromagnet

M. Fujihala, K. Morita, and T. Masuda

New insight into the spin behavior in an exotic state of matter puts us closer to next-generation spintronic devices. The quantum spin liquid (QSL) state is an exotic state of magnet where the spin of electrons, which generally exhibits order at low temperatures, remains disordered. Observation of a QSL state is one of the most important goals in condensed-matter physics. However, the QSL state in two-dimensional (2D) systems has not been clearly observed in real materials owing to the presence of site-mixing disorder or deviations from ideal models. The lack of a suitable model material exhibiting the QSL hinders observations of the QSL state in the 2D spin-1/2 systems.

Square-kagome lattice (SKL) magnet is known as the highly frustrated 2D system. There is a possibility that the QSL ground states are realized in the antiferromagnetic S = 1/2 Heisenberg model on SKL [1]. However, the lack of a model compound for the SKL system has obstructed a deeper understanding of its spin state. Motivated by the present status on the study of the SKL system, we



Fig. 1. (a) Crystal structure of KCu₆AlBiO₄(SO₄)₅Cl. Square-kagome lattice consisting of the Cu²⁺ ions with nearest-neighbor exchange coupling J_1 , J_2 , J_3 and next-nearest-neighbor exchange coupling J_X . (b) Crystal structure of KCu₆AlBiO₄(SO₄)₅Cl featuring a large interlayer spacing.



Fig. 2. (a) INS spectra at 5 K observed using HRC with an incident neutron energy of 45.95 meV. (b) INS spectra at 0.3 K observed using AMATERAS with incident neutron energy of 3.14 meV.

searched for compounds with the SKL containing Cu²⁺ spins, and synthesized the first compound of a SKL antiferromagnet, KCu₆AlBiO₄(SO₄)₅Cl, successfully [2]. As shown in Fig. 1(a), the SKL in the crystal structure of KCu₆AlBiO₄(SO₄)₅Cl comprises the Cu²⁺ ions. In each SK unit, the square is enclosed by four scalene triangles. From this crystal structure, it is recognized that KCu₆AlBiO₄(SO₄)₅Cl has three types of first neighbor interactions, J_1 , J_2 and J_3 , as shown in Fig. 1(a). By comprehensive experimental studies via magnetic susceptibility, magnetization, heat capacity, and muon spin relaxation, we confirm that the absence of magnetic long-range order down to 58mK, roughly three orders of magnitude lower than the NN interactions.

The quantum statistics of quasiparticle excitations depend on the type of QSL, in particular, the nature of their excitation. To grasp the whole picture of the spin excitation, we performed the inelastic neutron scattering (INS) experiments using the high-resolution chopper spectrometer HRC and cold-neutron disk chopper spectrometer AMATERAS installed in the MLF at J-PARC. As shown in Fig. 2(a), flat signals at around E = 10 and 7 meV are observed at 5 K. The signal due to magnetic excitation is generally enhanced at low-Q values, whereas phonon excitation is dominant at high-Q. The signals at around 10 and 7 meV increase with decreasing with Q, indicating that it comes from magnetic excitation. As shown in Fig. 2(b), streak-like excitation at Q = 0.8, 1.25, and 1.58 Å⁻¹ is clearly visible down to the elastic line, and its intensity increases continuously without signature of energy gap at least within the instrumental resolution. These INS data are consistent with a gapless continuum of spinon excitations. From the above, the flat signals at 10 and 7 meV probably indicate a van Hove singularity of spinon continuum edges at this energy.

Our experimental results strongly suggest the formation of a gapless QSL in KCu₆AlBiO₄(SO₄)₅Cl at very low temperature close to the ground state; however, they are inconsistent with the theoretical studies based on the J_1 - J_2 - J_3 SKL Heisenberg model. We calculate the dynamical spin structure factor $S(\mathbf{q}, \omega)$ in the SKL model with various values of the parameters, but we could not reproduce the INS experimental results. Therefore, in order to realize the QSL state in the SKL, we must impose an additional condition such as longer-range exchange interactions. Further experimental and theoretical study would reveal the conditions inducing the QSL state in SKL antiferromagnets.

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M. Fujihala^a, K. Morita^a, R. A. Mole^b, S. Mitsuda^a, T. Tohyama^a, S.

Yano^c, D.H. Yu^b, S. Sota^d, T. Kuwai^e, A. Koda^f, H. Okabe^f, H. Lee^f, S. Itoh^f, T. Hawai^f, T. Masuda, H. Sagayama^f, A. Matsuo, K. Kindo, S. Ohira-Kawamura^g, and K. Nakajima^g ^aTokyo University of Science ^bANSTO ^cNSRRC ^dRIKEN ^eUniversity of Toyama ^fKEK

gJ-PARC Center

Two-step Magnetic Anomaly in the High Field Magnetization Process in Yb_{1+x}In_{1-x}Cu₄

S. Yamanaka, A. Matsuo, and C. Michioka

The intermetallic compound YbInCu₄ exhibits a firstorder valence transition at 42 K under ambient pressure; Ytterbium ions have trivalent local moments in the hightemperature phase, and they become a mixed-valence state of an average valence of 2.9 in the low-temperature phase [1, 2]. In addition, a magnetic field-induced valence transition also occurs below 42 K with the transition field of \sim 30 T [3, 4]. To clarify the mechanism of the valence transition, substitution effects in Yb or In site have been extensively studied [3, 5]. Although this system was originally discovered as a solid solution RCu₂ without site-ordering, there are few reports on the substitution of In site by Yb itself on YbInCu₄. In this study, the magnetic and transport properties of Yb_{1+x}In_{1-x}Cu₄ are investigated using polycrystalline samples synthesized by the arc melting method, and the magnetic phase diagram in $Yb_{1+x}In_{1-x}Cu_4$ is investigated.

Figure 1 shows the temperature dependence of the magnetic susceptibility χ of Yb_{1+x}In_{1-x}Cu₄ measured in a magnetic field of 1 T. In a parent material, Yb_{1.01}In_{0.99}Cu₄, χ rapidly decreases below 42 K due to decrease in the effective valence of Yb ion from trivalent, which is consistent with the previous report [1]. The sharp magnetic anomaly accompanied by the valence transition in Yb_{1.01}In_{0.99}Cu₄ seems to change to a broad shape and shift to a higher temperature with increasing *x*. In all compositions, χ s obey the Curie-Weiss law above 150 K, and the values of the effective magnetic moment estimated from Curie-Weiss fits roughly agree with the calculated value for free Yb³⁺ ion, 4.54 μ B. This fact confirms that the valence state of Yb ions in the high-temperature phase is trivalent.

Figure 2 shows the temperature dependence of the



Fig. 1. Temperature dependence of the magnetic susceptibility χ of Yb_{1+x}In_{1-x}Cu₄ measured in a field of 1 T.

electrical resistivity ρ of Yb_{1+x}In_{1-x}Cu₄. In all compositions, ρ rapidly decreases below the valence transition temperature due to decrease in magnetic scattering accompanied by decrease in the localized moment of Yb³⁺. The valence transition temperature seems to shift to higher temperature with increasing *x*, consistent with behaviors of χ . For x = 0.21 and x = 0.25, ρ reaches a minimum value at approximately 40 K and then increases with decreasing temperature. These behaviors are typical in a metallic state with an impurity-Kondo-effect in which ρ shows -ln*T* dependence. It is natural to think that in the Yb-rich phase such as x = 0.21 or 0.25, all the Yb ions could not behave homogeneously and a part of Yb ions remain trivalent with an impurity moment.

Figure 3 shows the magnetization curve of $Yb_{1+x}In_{1-x}Cu_4$ measured at 4.2 K up to 72 T. For x = 0.16, 0.15, and 0.20, two-step magnetic anomalies are observed in the high field magnetization process. If this originates from phase separation, three or more steps would frequently appear. However, no such a behavior was observed in the results of more than 20 samples. In addition, the magnetization value for x = 0.16, 0.15, and 0.20 reaches 2 $\mu_{\rm B}$ after the first step and reaches 4 $\mu_{\rm B}$ after the second step. The fact that the similar behavior was observed in all three compounds suggests that the magnetic moments of the plateaux may be meaningful. Although the changes in the magnetic transition field by substitutions in YbInCu₄ have been reported, their magnetic transitions are all one step. The present observation of a successive phase transition in this system is the first time. The temperature dependences of χ and ρ do not show a behavior corresponding to the two-step anomaly. An intermediate phase is induced only by the magnetic field. The degen-



Fig. 2. Temperature dependence of the electrical resistivity ρ of $Yb_{1+x}In_{1-x}Cu_{4,.}$



Fig. 3 Magnetization curves M -H of Yb_{1+x}In_{1-x}Cu₄ measured at 4.2 K up to 72 T.

erated ground state of Yb³⁺ (²F_{7/2}) is split by the crystal electric field (CEF) effects, and each state has a different saturation magnetization. In x = 0.16, 0.15, and 0.20, the lower transition field induces the trivalent state however the magnetic moment is limited by CEF. Subsequently in the higher transition field, the Zeeman- energy exceeds CEF and induces a full saturation magnetization of Yb³⁺ of 4 μ_B . For x = 0.01 and 0.10, the magnetization reaches about 4 μ_B in a one-step transition without an intermediate phase. This is probably because CEF of small substituted compounds is smaller than the magnetic transition field which induces the trivalent state.

In conclusion, we discovered the successive magnetic transition in the magnetization process in $Yb_{1+x}In_{1-x}Cu_4$ (x = 0.15, 0.16, and 0.20) and proposed that it originates from competition and corporation of the Zeeman energy, CEF effect and magnetic interactions.

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Authors

S. Yamanaka^a, T. Nakahigashi^a, C. Michioka^a, H. Ueda^a, A. Matsuo, K. Kindo, and K. Yoshimura^a ^aKyoto Unuversity

Origin of Inverse Magnetocaloric Effects in Ni-Mn-based Heusler Alloys

T. Kihara, X. Xu, and M. Tokunaga

The development of heat-exchange systems using the magnetocaloric effect is a topic where material science can solve energy problems. The magnetocaloric effect has long been used to realize ultra-low temperature using the adiabatic demagnetization procedure. This effect was recently expected for heat exchangers with higher efficiency than conventional gas-compression/expansion systems [1]. However, most of the materials that exhibit significant magnetocaloric effect contain heavy rare-earth elements, so that the high cost of the materials hinders their practical use. We have studied thermodynamic properties of Heusler alloys without rare-earth elements to realize the giant magnetocaloric effect involving the entropy of the lattice and electronic systems [2-5].

Ni-Mn-based Heusler alloys have attracted considerable attention as magnetic shape memory alloys [6]. In our previous work on Ni-Co-Mn-In alloys, we directly observed prominent negative magnetocaloric effects at the fieldinduced phase transitions from paramagnetic martensite to ferromagnetic austenite phase. From the systematic highfield studies of magnetocaloric effect, magnetization, heat capacity, and microscopy, we concluded that this effect originated from the increase of lattice entropy associated with the structural phase transition [2].

In the present study, we measured the magnetization,

magnetocaloric effect, and magnetostriction of Ni-Co-Mn-Ga alloys in pulsed high magnetic fields up to 56 T [4, 5]. As shown in Fig. 1(a), metamagnetic transitions similar to those in the Ni-Co-Mn-In alloy were observed in this material. Magnetostriction measured on a polycrystal-line sample using the capacitance method [7] showed a significant lattice distortion associated with this transition [Fig. 1(b)], suggesting that this magnetic transition is accompanied by a structural phase transition from the martensite to the austenite phase.

The change in the sample temperature at the magnetic field-induced phase transition shows a negative magnetocaloric effect, as shown in Fig. 2. In contrast to the Ni-Co-Mn-In alloy, the negative magnetocaloric effect shows up even after completing the field-induced magnetic and structural transition. The experimental results of heat capacity and theoretical results of first-principles calculation show that the electronic specific heat coefficient increases significantly at the transition to the austenite phase: the entropy of the electron system plays an essential role in the magnetocaloric effect of this system. The increase in lattice and electronic entropy associated with the magnetic field-induced phase transition dominates over the decrease in the spin entropy change, which shows up as a negative magnetocaloric effect that decreases the sample temperature in a magnetic field. If we can incorporate these entropy changes in the same sign, we expect magnetocaloric effects beyond the limit of the spin system. Microscopic discussion in the present study will pave the way for this giant magnetocaloric effect.

Most of the previous studies on magnetocaloric materials have focused on their properties in the magnetic field region below 5 T. In the future society where hydrogen energy and high-temperature superconducting cables are put to practical use. In this situation, large-scale application of the magneto-



Fig. 1. (a) Field-dependence of magnetization in a polycrystal of $Ni_{41}Co_9Mn_{31.5}Ga_{18.5}$ at several temperatures. Steep increase in magnetization indicates emergence of metamagnetic transitions. (b) Longitudinal magnetostriction of $Ni_{41}Co_9Mn_{31.5}Ga_{18.5}$ measured at 290 K. The inset shows schematics of the capacitance method. Prominent increase of the sample length corresponds to the structural transition from the martensite to the austenite phase simultaneously with the metamagnetic transition.



Fig. 2. Magnetocaloric effect of Ni₄₁Co₉Mn_{31.5}Ga_{18.5} studied in adiabatic magnetization process realized in pulsed magnetic fields. Instantaneous change in sample temperature is detected using a thinfilm resistive thermometer attached to the sample. In addition to steep reduction of temperature at the metamagnetic transition ($\Delta T_{\rm IMT}$) further negative magnetocaloric effect is observed at higher fields (ΔT^*)

caloric effects using large superconducting magnets, such as gas liquefaction projects, will also be important. The evaluation of the magnetocaloric effects in Heusler alloys at high magnetic fields provides an essential hint for solving energy problems in near future.

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T. Kihara^a, T. Roy^a, X. Xu^a, A. Miyake, M. Tsujikawa^a, H. Mitamura, M. Tokunaga, Y. Adachi^b, T. Eto^c, and T. Kanomata^d ^aTohoku University ^bYamagata University ^cKurume Institute of Technology

^dTohoku Gakuin University

Observation of In-Plane Magnetic Field Induced Phase Transitions in FeSe

J. S. Kim, Y. Kohama, and J. M. Ok

In conventional superconductors, spin polarization can destroy superconductivity when Zeeman energy surpasses the binding energy of Cooper pairs, known as the Pauli paramagnetic limit. Beyond the Pauli limit, exotic superconducting phases, often coexisting with complex magnetic orders, have been observed in some unconventional superconductors. Even in these cases, however, field-induced spin imbalance is usually at most a few %. So far, realization of the highly spin-imbalanced superconductivity and possible field-induced exotic phases have been remained elusive, partly due to the lack of the suitable material candidates.

FeSe is a promising candidate hosting a strongly spin imbalanced state at high magnetic fields. The observed in-plane upper critical field of FeSe is $H_{c2}^{ab} \approx 25$ T, well above the conventional BCS value of the Pauli limiting field $H_P \approx 15.6$ T ($H_P = 1.84$ T_c), and the Zeeman energy at H_{c2} becomes comparable with the superconducting gap Δ_{SC} ($\mu_B H_{c2} \sim \Delta_{SC}$). In addition, high-quality FeSe single crystals are found to be in the clean limit with a much longer mean free path *l* than the superconducting coherence length ξ ($l >> \xi$). More importantly, FeSe is in the so-called BCS-BEC (Bose-Einstein condensate) crossover regime $(\Delta_{SC} \sim E_F)$ with exceptionally small Fermi energies. The spin imbalance reaches up to $\sim 40\%$ for one of the Fermi surfaces (FSs) at $H_{c2}^{ab} \approx 25$ T, much larger than the typical value of a few % in other superconductors. Therefore, FeSe can be a model system to study whether, and if so how, competing magnetic or superconducting instabilities trigger exotic fieldinduced phases in multiband superconductors with a large spin imbalance.

In this work, using torque magnetometry, specific heat, and magnetocaloric measurements, we identified successive anomalies with increasing in-plane magnetic field, below H_{c2} at low temperatures and in the clean limit. The signatures of unusual phase transitions below H_{c2}^{ab} and below $T^* \approx 2$ K are observed in the field-dependent torque magnetometry τ (H). The torque magnetometry in superconductors usually exhibits a typical saw-tow shaped curve of the field derivative τ (H), $d\tau/dH$ due to vortex pinning. In FeSe, however, we observed two additional anomalies at $H_1 \sim 15$ T and $H_2 \sim 22$ T, well below the irreversible field H_{irr} at which the hysteresis in τ (H) starts to develop (Fig. 1a and 1b). The transition fields H_1 and H_2 follow the distinct dependence on temperature or field angle from those of $H_{\rm irr} \approx H_{\rm c2}$ (Figs. 1a and 1c). Upon increasing temperature or the tilting angle of the magnetic field (θ) from $H \parallel ab$, H_{irr} systematically decreases, similar to H_{c2} . In contrast, the anomalies are pronounced only at low temperatures below T^* and near $H \parallel ab$ with $\theta \leq 15^{\circ}$. Also, the transition fields H_1 and H_2 remain almost the same with variation of temperature or field angle (Figs. 2a and 2b). The anomalies seen in torque magnetometry are further confirmed by magnetocaloric and specific heat measurements [1]. These findings clearly evidence the presence of field-induced phases near the in-plane magnetic fields below H_{c2}^{ab} .



Fig. 1. (a) Magnetic field dependent torque τ (*H*) close to *H* || *ab* at various temperatures. The irreversibility field at $H_{irr} \sim 25$ T and anomalies at $H_1 \sim 15$ T and $H_2 \sim 22$ T are indicated by black, red and blue arrows, respectively. (b) The field-derivative curve $d\tau(H)/dH$ showing clear anomalies at H_1 and H_2 . (c) Magnetic field dependent torque τ (H) at various field angles.



Fig. 2. (a,b) Magnetic phase diagram of FeSe for H || ab as a function of temperature (a) and field orientation (θ) with respect to the abplane (b). The upper critical field $H_{c2}a^{b}$ (T) (open symbols) are determined by resistivity (black open circle), TDO frequency (black open diamond), and torque magnetometry (black open star) measurements, while the field-induced phase transitions at H_1 and H_2 are obtained by torque magnetometry (colored open star) and the magnetocaloric effect (colored solid triangle). The inset shows schematics of the possible nesting effect via $q = (0, \pi)$ or (π, π) between the spin-split Fermi surfaces (FSs) with anisotropic superconducting gap (gray shade). Near H_1 , the nesting effect is expected between two FSs with opposite spins via a SDW momentum $q = (\pi, \pi)$ (bottom), while the nesting with q = $(0, \pi)$ is expected near H_2 between two FSs with the same spins (top).

One possible candidate for the high field anomalies is then the FFLO phase. In this case, the Cooper-pair state $(k \uparrow, -k+q \downarrow)$ is formed with a momentum mismatch (q) between the spin-split FSs. In multiband superconductors, each FS has its own FFLO instability with a different modulation length q_i^{-1} (*i*, band index), and these instabilities compete with each other, inducing the multiple FFLO orders at different magnetic fields. Alternatively, the spin-density wave (SDW) phase of field-induced quasiparticles can be another promising candidate. When the superconductivity is suppressed by Pauli pair breaking near the superconducting gap nodes or minima, the SDW order can be triggered by the nesting effect by field-induced quasiparticles. Due to an exceptionally small $E_{\rm F}$, the Zeeman effect results in the spin-split FSs much different in size, which significantly affects the nesting condition in FeSe. We found that the nesting via $q = (\pi, \pi)$ nicely matches the two different FSs with opposite spins at $H\sim 16$ T, and with the same spins at $H\sim22$ T (Fig. 2b). in good agreement with the observed transition fields, H_1 and H_2 . The incipient spin fluctuations and strong coupling between the field-induced quasiparticles may allow the coexisting phase with the SDW and superconductivity.

In the current stage, the detailed nature of the fieldinduced phase transitions, including possible coexistence of the SDW and the FFLO orders, remains to be clarified. Nevertheless, these observations clearly demonstrate that FeSe offers a unique system, in which field-induced phase transitions occur in the superconducting state. This poses a challenge to our understanding on the complex interplay between anisotropic superconducting order, incipient magnetic instabilities, and the multi-band effect in the largely spin-imbalanced superconducting systems.

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J. M. Ok^a, C. I. Kwon^a, J. S. You^a, S. K. Park^a, K.-S. Kim^a, J. S. Kim^a, Y. Kohama, K. Kindo, J.-H. Kim^b, Y. J. Jo^b, E. S. Choi^c, W. Kang^d, E. G. Moon^c, and A. Gurevich^f ^aPohang University of Science and Technology ^bKyungpook National University ^cNational High Magnetic Field Laboratory ^dEwha Womans University ^eKorea Academy Institute of Science and Technology ^fOld Dominion University

Hydrogen-Bonded Structure of Water Responsible for Ion Selective Permeability of Self-Assembled Liquid Crystalline Polymer Membranes

T. Kato and Y. Harada

Liquid crystals (LC) are appealing for nanofiltration membranes with uniform subnanopores which enable efficient and thermally stable filtration and ion selectivity [1]. Many principles of water filtration are intuitive: particles bigger than the pore size cannot pass through a membrane, and electrostatic interactions between ions, water molecules and the membrane can aid the process. However, the permeability of these LC membranes is higher for larger, dianionic SO_4^{2-} ions than it is for monoanionic, smaller Cl⁻ ions, which could not be explained using the common filtration principles, which implies the presence of another driving force for ion selectivity. One of such possibility is the structure of the water surrounding the ions

Here we investigated the hydrogen-bonded configuration of water molecules in the subnanopores of a bicontinuous cubic LC membrane formed by in-situ polymerization of compound 1 (Fig. 1a), and how it affects the permeation of dianionic $SO_4^{2^-}$ and monoanionic Cl⁻[2]. We used highresolution X-ray emission spectroscopy (XES) [3] to learn



Fig. 1. (a) Molecular structure of an LC monomer (1). The monomers were self-assembled to form a bicontinuous cubic (Cub_{bi}) LC structure through which ions are selectively transported. (b) Schematic image of soft X-ray emission detection from water in the LC membrane.



Fig. 2. Valence electronic structure of H₂O in (a) the LC membrane, (b) 1.0 mol/l and 2.5 mol/l MgSO₄, (c) 1.0 mol/l and 3.0 mol/l NaCl aqueous solutions.

how water arranges itself in the subnanopores.

XES spectra of pure liquid H₂O absorbed in the LC membrane and hydrating water of permeating solutes, MgSO₄ and NaCl were collected at the SPring-8 BL07LSU HORNET station using a high-resolution XES spectrometer [4]. A custom-made ambient pressure cell was used to expose the LC membrane to humidity-controlled moisture and nitrogen as a carrier gas. (Fig. 1b). To explore the origin of the selective ion permeation (73±5% for MgSO4 and 30±6% for NaCl), hydrogen-bonded structures of H₂O in the LC membrane were compared with those in the MgSO₄ and NaCl hydrations. Spectra of water within the subnanopores (Fig. 2a) revealed that its hydrogen-bonded network, when confined, loses some structural features characteristic of bulk water in favor of new structural features. Very similar structural features are observed in the spectra of the hydration shell of SO₄²⁻ (Fig. 2b) but not in that of Cl⁻ (Fig. 2c). We interpret this as the reason for the greater membrane permeability of SO₄²⁻ than that of Cl⁻. In the near future computational studies might help understand the exact structure of the hydrogen-bonded network within the subnanopores. The nature of hydrogen-bonded networks becomes an additional parameter that should be considered and controlled to obtain highly efficient water filtrations.

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R. Watanabe^a, T Sakamoto^a, K. Yamazoe, J. Miyawaki, T. Kato^a, and Y. Harada