# Joint Research Highlights

# Heavy Fermion State of YbNi<sub>2</sub>Si<sub>3</sub> without Local Inversion Symmetry

### S. Nakamura, T. Sakakibara, and M. Yamashita

Various fascinating phenomena often appear in the materials without the global inversion symmetry. It is theoretically suggested that both global and local inversionsymmetry-breaking host an exotic superconductivity. This study focuses on the materials in which only the local inversion symmetry is broken. There are not much examples showing superconductivity in the materials without the local inversion symmetry, but the local inversion symmetry is broken in high temperature superconductors such as ironbased and copper-oxide superconductors.

We discover a new heavy-fermion compound YbNi<sub>2</sub>Si<sub>3</sub> in which the local inversion symmetry at ytterbium site is broken (Fig. 1(a) and (b)), whereas the global inversion symmetry is retained. The space group of this material is I4/*mmm*, and the site symmetry at Yb-ion is 4*mm*. This crystal structure is partially similar to tetragonal ThCr<sub>2</sub>Si<sub>2</sub>-type crystal structure; CeCu<sub>2</sub>Si<sub>2</sub> and URu<sub>2</sub>Si<sub>2</sub> are well known as heavy-fermion superconductors. Rare-earth metal, transition metal, and silicone atoms form a square lattice on the *c* plane both in these two crystal structures.

The electrical resistivity, the magnetization, the magnetic torque and the heat capacity measurements have been performed in YbNi<sub>2</sub>Si<sub>3</sub>, and we check if there is a superconducting state without the local inversion symmetry. We



Fig. 1. (a) The crystal structure of YbNi<sub>2</sub>Si<sub>3</sub> in which the local inversion symmetry around the Yb ions is broken as shown in (b). (c) The *H*-*T* phase diagram, where  $T_{\rm N}$  and  $T_{\rm max}$  denote the Néel temperature and a crossover line between paramagnetic and forced ferromagnetic regions, respectively.



Fig. 2. (a) The temperature dependence of the heat capacity of  $YbNi_2Si_3$  at zero magnetic field. (b) The magnetic field dependence of the magnetic torque of  $YbNi_2Si_3$  at 208 and 2 mK.

determine the H-T phase diagram of YbNi<sub>2</sub>Si<sub>3</sub> by the magnetization and the heat capacity measurements (Fig. 1(c)). We find an antiferromagnetic state appears below 0.35 K at zero magnetic field, and it is suppressed by applying a magnetic field of 0.7 T. The temperature dependence of the electrical resistivity shows a typical heavy-fermion behavior with the Kondo temperature of ~ 2 K. Remarkably, a large electronic specific heat coefficient of  $\gamma = 5$  J/mol K<sup>2</sup> is found to remain down to 0.08 K in the antiferromagnetic state (Fig. 2(a)), demonstrating a heavy-fermion state in YbNi<sub>2</sub>Si<sub>3</sub>. Such large entropy is often released by a superconducting transition at a lower temperature. To this end, we have carried out the magnetic torque measurements down to ultralow temperatures. However, no discernible change is observed down to 2 mK (Fig. 2(b)), showing the persistence of the heavyfermion state. We further check the valence state of the Yb ions via hard X-ray photoemission spectroscopy, and find that almost all the Yb-ions are in the Yb<sup>3+</sup> state, showing the absence of the valence fluctuation between  $Yb^{2+}$  and  $Yb^{3+}$ . This absence would suggest that the origin of the heavyfermion state is a magnetic fluctuation rather than a valencefluctuation, which often expected in Yb compounds. It remains as a important future issue to reveal the origin of the heavy-fermion state in YbNi2Si3 by microscopic measurements such as NMR.

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# Patterning of Topological Insulator on Thin Film

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Because topological insulators (TIs) have their conducting channels at the sample edges, shapes of them play crucial roles in device applications. Hence it can be a very convenient tool if we can "draw" spatial patterns of TI just like drawing a picture. Members of two-dimensional (2D) transition metal dichalcogenides (TMDCs) have been predicted and experimentally confirmed as a new class of 2D TI materials though the edge conduction is fragile in most cases. Here, we realize the controlled patterning of a TI phase embedded in an insulating phase of thin molybdenumdisulfide (MoS<sub>2</sub>) by laser beam irradiation.

 $MoS_2$  is known to have various metastable lattice structures according to the freedom in the stacking angle of the chalcogen layer. In so called H-phase, the chalcogens form triangle poles or trigonal prism. In single crystal, two-layers form a unit and called 2H phase. This is semiconducting.

In so called T-phase, the two-triangles are in the twisted relation. The stacking unit is single and called 1T phase. This is metallic. These two are the representative phases but there are many other metastable phases.

An interesting is the one called 1T' phase, which is somewhat intermediate between these two. In this 1T' phase, for example this upper chalcogen atoms shift in this way and stop at some intermediate position. Some theories predict this 1T' phase should be a topological phase. So if we can cause local phase transition between these three, we can make up desired circuits with semiconductors, metals and topological insulators. We showed that 1T' phase can be actually created in 2H  $MOS_2$  and also it works as a TI [1].

In order to obtain 1T', we used the excitation by Ar laser beam of energy 2.5 eV and simply drew some patterns on 2H MoS<sub>2</sub>. From an atomic force microscope topography, it



Fig. 1. (a) X-ray photoelectron spectroscopy taken at a laser-irradiated region (black line). Red and blue lines are those expected for 1T' and 2H phases respectively.(b) Raman shift spectra. Blue: 2H phase before laser irradiation. Red: mixture of 1T' phase and 2H phase after irradiation.



Fig. 2. Resistance of laser irradiated pattern on  $MoS_2$  as a function of back gate voltage. In the inset we illustrate the setup of resistance measurement.

turned out that the irradiated region is a bit thinner than the surrounding region. This is probably due to some evaporation of atoms and the phase transition is not due to the direct energy transfer from photon to lattice but some heating effect causes the transition. The appearance of 1T' phase was confirmed in the Raman and the XPS spectra as shown in Fig. 1 (a) and (b).

The pattern of 1T' phase we used for the measurement of edge channel conduction is a simple H-shape as illustrated in the inset of Fig. 2. The size is about 2  $\mu$ m, which is comparatively large compared with ordinary reported coherence length of edge conductions in TIs. The flake of MoS2 was placed on a metallic doped Si substrate covered with SiO<sub>2</sub>, hence we can tune the position of Fermi energy in MoS<sub>2</sub> wtih the back gate voltage. Figure 2 shows the resistance of H-shaped sample in the measurement geometry drawn in the inset, as a function of the back gate voltage. The resistance R took a peak structure around at  $R = R_q/2 = h/2e^2 =$ 12.6 k $\Omega$ . This is the value calculated for ideal helical edge states and clearly tells that the patterned 1T' was working as a TI. The resistance quantization persisted surprisingly up to room temperature manifesting an opening of large spin-orbit energy gap. The gap closing around the sample edges was also confirmed with a scanning tunneling spectroscopy.

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# Electronic Structures of 4°-Twisted Bilayer Graphene Fabricated in a Vacuum

### S. Tanaka and F. Komori

Twisted bilayer graphene (TBG) is a stacked two graphene sheets with mutually in-plane rotation, and exhibits electronic states different from those observed in a typical bilayer graphene with Bernal stacking. Its Fermi velocity in the vicinity of the Dirac point strongly depends on the twistangle  $\theta$  below 10° [1], and vanishes around a magic angle of  $\theta \sim 1.1^{\circ}$  [2]. At this magic angle, a flat band with extremely sharp density of states is thus realized, and its electronic



Fig. 1. (a) LEED pattern at the area with TBG. Bright 12 spots are identified as two sets of 6-fold symmetric graphene diffraction spots from the lower ( $g_{CVD}$ ) and upper ( $g_{tr}$ ) layers. Inset shows the magnified image of the graphene diffraction including satellite spots (circles) due to the moiré structure. (b) STM image taken at the TBG area, showing graphene atomic image and moiré lattices. Moiré unit cell of the lattice is indicated by arrows. The image was taken at the sample bias voltage 0.8 *V* and tunneling current 0.5 nA at 80 K [3].

properties have attracted much attention. TBG is usually prepared by stacking mechanically-exfoliated graphene sheets in air, and thus it is difficult to prepare a millimeterscale samples with clean interface between the sheets for using standard surface analysis techniques such as various diffraction methods and high-resolution photoemission spectroscopy. To prepare wide TBG's with clean interface, we have developed a new method of directly bonding clean graphene sheets in a vacuum without any chemical adhesion and transmission media. For this purpose, we use monolayer graphene that can be easily exfoliated from the SiC substrate [3]. The band structure observed by angle resolved photoemission spectroscopy (ARPES) exhibits changes of the electronic states due to the interlayer interaction [1].

Graphene sheets are made on a 4H-SiC (0001) substrate



Fig. 2. ARPES constant energy and band dispersion maps. The  $k_x$  axis is on the line between the middle of the two K points of the graphene layers ( $K_{CVD}$ ,  $K_{tr}$ ) and  $\Gamma$  point. (a) Constant energy maps at  $E_F$  without (left) and with (right) image enhancement. Replica bands are seen at this energy as in left. (b) Band dispersions along  $k_y$  axis at  $k_x = 1.695$ Å<sup>-1</sup> (left) and along  $k_x$  axis at  $k_y = -0.069$ Å<sup>-1</sup> (right). Here, the ARPES intensity is normalized by the Fermi-Dirac distribution function at 300 K. Two Dirac bands of the transferred graphene are seen at negative  $k_y$ in the left figure [3].

by chemical vapor deposition (CVD) using ethylene. A buffer layer with a 3 × 3 periodicity is formed at the interface between the graphene and substrate, and allows us to exfoliate the graphene layer easily. It is noted that graphene on the thermally decomposed  $6\sqrt{3} \times 6\sqrt{3}$  -R30° buffer layer (6R3) coexists. The TBG samples are prepared at 200 °C in a vacuum by pressing together for 1 hour and detached at the same temperature. The samples were then evaluated by optical microscope,  $\mu$ -Raman spectroscopy, low energy electron diffraction (LEED), scanning tunneling microscopy (STM) and ARPES. Sub-millimeter areas with TBG were confirmed on the substrate.

Observed LEED and STM images of a 4°-rotated TBG are shown in Fig. 1. Two sets of 6-fold bright graphene spots with surrounding satellite spots are seen in Fig. 1(a), and correspond to lower-layer (g<sub>CVD</sub>) and upper-layer transferred (gtr) graphene. In the STM image, a moiré pattern due to the twisted layers is observed with the graphene lattice. The twist angle  $\theta$  is estimated from the satellite-spot periodicity and the moiré image. Graphene band structures measured by ARPES at 300 K using 52 eV synchrotron light (KEK-PF, BL13) are shown in Fig. 2. Two graphene Dirac cones appear at Fermi energy  $(E_F)$  as in Fig. 2(a). The band structure shown in Fig. 2(b) indicates the both graphene layers are p-doped. The cone at negative  $k_v$  originates from the transferred graphene on the  $3 \times 3$  substrate. In addition, an n-doped Dirac band is seen in Fig. 2(b), which originates from the transferred graphene on the 6R3 substrate. Energy gap of the bands due to the interlayer interaction is found at  $k_v = 0$  in the same figure. The Dirac band shown in Fig. 2(b, right) has a kind structure at 0.2 eV.

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# Pulsed Laser Deposition with Rapid Target Switching

## Y. Matsumoto and M. Lippmaa

Pulsed laser deposition (PLD) is one of the most common techniques for growing complex oxide thin films. The biggest merit of PLD is the near-stoichiometric transfer of material from a polycrystalline ceramic target to a singlecrystalline thin film, which means that it is usually not necessary to tune individual cation ratios during the crystal growth process. Indeed, PLD became the method of choice for developing high-temperature superconductor thin films and devices due to the simplicity of phase and stoichiometry control.

The PLD process is based on the use of a high-intensity pulsed laser that momentarily heats the surface of a ceramic source material pellet, forming a rapidly expanding plasma cloud in vacuum or in a low-pressure reactive gas ambient. Due to the pulsed nature of the process, the surface of a growing film reaches a high level of supersaturation when the plasma plume arrives, but this very high instantaneous deposition rate is followed by a long relaxation period of up to about a second. The dynamic aspect of the crystal growth is therefore also important in determining the growth mode and crystallinity of a film.

In recent years, there is increasing interest in materials property mapping and the use of combined computational and experimental materials data to feed machine learning models for aiding materials discovery and optimization. In thin film property mapping experiments, it is necessary to grow large numbers of thin film samples with slightly different compositions. In a traditional PLD process, this would require the synthesis of a large number of bulk compositions for use as PLD ablation targets, which is technically difficult. Multi-target PLD has been used to avoid this problem by using just two ablation targets to grow mixed-composition phases. For example, by alternating ablation from SrTiO<sub>3</sub> and BaTiO<sub>3</sub> targets, it is possible to grow any intermediate composition in the Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> phase space. Since each unit cell layer usually requires up to a hundred ablation pulses to grow, it is easy to adjust compositions on a percent scale. However, switching between two targets generally requires mechanical motion of the target stage, which is a slower process than the normal ablation pulse period. Since adatom surface migration during the interpulse period affects the film microstructure, the longer time delay of target exchange may lead to a nanoscale multiphase film of, e.g., SrTiO<sub>3</sub> and BaTiO<sub>3</sub> domains instead of a mixed Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> crystal.

In this project, supported by the Joint Use program, a rapid beam deflection system was developed to switch ablation between two target materials on a millisecond scale. [1] The experimental setup is illustrated in Figs. 1(a,b). A galvanometer mirror is used to direct ablation laser pulses on one of two targets without having to move the target stage. The mirror motion is fast enough to interleave depositions



Fig. 1. (a) Photograph of the ablation target stage, showing the ablation spot on the lower target. (b) Schematic diagram of the rapid galvanometer beam switching between two targets. (c) Design (blue) and measured (red) composition of a  $(Ba,Sr)TiO_3$  film. The x-ray diffraction pattern in (d) shows that the film lattice parameter varied continuously in the film.

from two targets in a 1:1 pulse sequence at laser pulse rates of up to 200 Hz.

Various film synthesis experiments were used to test the benefits of rapid sequential deposition of various mixedcomposition oxide films. The experiments clearly showed the benefit of rapid target switching in synthesizing (Ba,Sr)TiO<sub>3</sub>, (Bi,Sm)FeO<sub>3</sub>, (Mg,Zn)O, Ni-Ge, and Ni-Si films. A particularly interesting capability of this new rapid target switching PLD system is depth direction grading of film composition for tuning the lattice parameter, doping level, crystal symmetry, or other properties without sacrificing the deposition rate or risking phase segregation when slower mechanical target stage motion is used for multi-target deposition.

An example of a depth-graded  $Ba_{1-x}Sr_xTiO_3$  film composition is shown in Fig. 1(c). The Ba content was adjusted over the 100 nm thickness of the film from 0 to 30% as shown by the design plot (blue) and verified by Secondary Ion Mass Spectrometry (SIMS) as shown in red. The continuous change of the lattice parameter can be seen in the x-ray diffraction pattern for a gradient film grown on a SrRuO<sub>3</sub> electrode layer on a SrTiO<sub>3</sub> substrate. The spread of the (Ba,Sr)TiO<sub>3</sub> film peak corresponds to the continuous composition gradient in the film. This type of gradient films can be used in novel types of photoelectrochemical electrodes and for constructing polar films with an internal electric field gradient related to the depth-variable polarization of the lattice.

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# Density Functional Theory with Machine Learned Functional

### R. Nagai, R. Akashi, and O. Sugino

Modern electronic structure theory of materials is most frequently based on the Kohn-Sham density functional theory (KS-DFT), where the accuracy depends on the quality of the density-to-energy mapping called exchangecorrelation (xc) functional. The mapping has extremely large degrees of freedom that are too complex to determine manually. In this context, we have proposed a machine learning approach [1]. We have prepared the atomization energy  $(E_a)$  and electron density  $n(\mathbf{r})$  of reference molecules using a quantum chemical simulation and let neural network (NN) learn the data. In the learning, the energy  $E_a$  and the density  $n(\mathbf{r})$  are related via a functional of the density called the xc potential  $\varepsilon_{xc}[n](\mathbf{r})$ , and the parameters characterizing the functional are optimized to best reproduce the input data. The mapping thus established depends on the form of the functional, such as the point-to-point mapping called local density approximation (LDA) and the mapping reinforced using the density gradient called generalized gradient approximation (GGA) or meta-GGA. Quality of the functionals was tested for a ten dozen of unreferenced molecules and was found superior to existing ones for each form, suggesting possibility to systematically develop accurate functionals.



Fig. 1. Machine learning scheme for developing exchange correlation (xc) functional. Referring to electron density n(r) and atomization energy  $E_a$  of a few molecules, the xc energy was related to the density as a functional  $\varepsilon_{xc}[n](r)$ . With this machine learned functional, n(r) and  $E_a$  of unreferenced materials were found to be predicted more accurately than with conventional functionals.

In our study, we have used three molecules,  $H_2O$ ,  $NH_3$ , and NO, that contain different bonding property and spin polarization, as the reference. The NN successfully determined the parameters without overtraining owing large number of data contained in the density, which amounts to 100,000. We further tried to include nonlocality into the functional beyond the gradient approximations by considering the electron density averaged in the vicinity of an electron. The resulting functional form, called near region approximation (NRA), improves the accuracy equivalent to that achieved using the nonlocal exchange, allowing thereby significantly to reduce the computational complexity.

In view of the ability of artificial intelligence to recognize a picture, it is likely to be possible to learn the chemical bonds without explicitly indicating a descriptor. Such advance in the method will enable a researcher to develop a high-quality functional dedicated to the target materials of interest with an effect of speed-up of material design. Impact of systematic functional development is thus expected to be large in the computational materials science.

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# Predicting and Understanding Structural Phase Transition of Solids from Finite-Temperature Phonon Calculations

# T. Tadano and W. A. Saidi

The study of structural phase transition has been an active research subject in condensed matter physics and materials science because a variety of materials' properties, including but not limited to transport, optical, and superconducting properties, often changes sensitively with the crystal structure. So far, first-principles calculations based on density functional theory (DFT) have been performed extensively for identifying (meta-)stable structures at T = 0 K. On the other hand, predicting finite-temperature structures based on DFT is still challenging because it requires a proper treatment of entropic effects of phonons and magnons. In particular, the vibrational entropy plays a central role in realizing structural phase transitions of nonmagnetic materials, including perovskite oxides such as BaTiO<sub>3</sub>. However, the conventional phonon calculation method based on the harmonic approximation (HA) often yields unstable phonon modes for high-temperature phases of phase change materials, which hinders an estimation of vibrational entropy.

To overcome the limitation of the conventional phonon calculation method, we have recently developed a new approach that is applicable to high-temperature phases [1]. Our method is based on the self-consistent phonon (SCP) theory, which incorporates the anharmonic renormalization of phonons at the mean-field level. We have so far employed the developed SCP scheme to compute finite-temperature phonons of cubic SrTiO<sub>3</sub> [1], thermoelectric clathrate [2], and ScF<sub>3</sub> [3], where we have obtained an excellent agreement with the experimental data. Also, it can be used to compute the vibrational free energy of solid whose structure is dynamically unstable within the HA, as has been demonstrated for ScF<sub>3</sub> [3] and hydrogen-rich superconductors [4].

To further test and improve the prediction accuracy of our approach, we have recently applied the SCP method to an all-inorganic halide perovskite CsPbBr<sub>3</sub>, which has been actively studied in recent years as an efficient photovoltaic material. CsPbBr3 shows a successive structural phase transition with cooling from cubic  $\alpha$  phase  $(Pm\bar{3}m)$  to the tetragonal  $\beta$  phase (P4/mbm) at 403 K and then to the orthorhombic y phase (Pnma) at 361 K. When the HA was used, we obtained unstable phonon modes for the high-temperature phases as shown in Fig. 1. These phonon modes involve a distortive motion of the bromine octahedra; therefore, these soft modes, particularly those at the M (1/2,1/2,0) point of the  $\alpha$  phase and the Z (0,0,1/2) point of the  $\beta$  phase, may act as the soft modes of the structural phase transition. After including the effect of finite-temperature renormalization by the SCP theory, all phonon modes were stabilized, as shown by solid lines in Fig.1. After that, we calculated the vibra-



Fig. 1. (Top) Crystal structures of  $\alpha$ ,  $\beta$ , and  $\gamma$  phases of halide perovskite CsPbBr<sub>3</sub>. (Bottom) Phonon dispersion curves of three different phases of CsPbBr<sub>3</sub> calculated within the harmonic approximation (dotted lines) and self-consistent phonon method at 500 K (solid lines). The unstable phonon modes in the high-temperature phases ( $\beta$ ,  $\gamma$ ) are stabilized by anharmonic renormalization at finite temperature.

tional free energies with including the effect of the quartic anharmonicity [3] and predicted the phase transition temperature ( $T_c$ ) based on the calculated Helmholtz free energies. When we used the PBEsol exchange-correlational functional, the  $T_c$  values of the cubic-to-tetragonal and tetragonal-toorthorhombic phase transitions were predicted as  $T_c \sim 280$ K and  $T_c \sim 180$  K, respectively, both of which underestimate the experimental results. To improve the prediction accuracy, we have further considered the higher-order correction to the vibrational free energy that originates from the cubic anharmonicity. Then, the  $T_c$  value of the cubic-to-tetragonal phase transition changed as  $T_c \sim 400$  K, which shows better agreement with the experimental value.

We are also interested in how the structural phase transition affects thermal transport properties. To investigate this point quantitatively, we have calculated the lattice thermal conductivity of CsPbBr3 for the three different phases. To this end, we calculated the phonon lifetimes by considering the three-phonon scattering process on top of the SCP calculations. After that, the lattice thermal conductivity was estimated, where both of the particle-like transport and coherent transport terms were calculated following Ref. [5]. For all phases, the thermal conductivity values were smaller than 1 W/mK, indicating the strong lattice anharmonicity of CsPbBr<sub>3</sub>. We found that the lattice thermal conductivity of the high-temperature  $\alpha$  phase was larger than those of the low-temperature phases due to the longer phonon lifetimes in the highly symmetric  $\alpha$  phase, which can be attributed to the smaller scattering phase space of the three-phonon process. Interestingly, unlike the conventional semiconductors where most of the thermal transport is accounted for by the highly dispersive acoustic phonons, more than ~60% of the total thermal conductivity was carried by optical phonons above  $30 \text{ cm}^{-1}$  in CsPbBr<sub>3</sub>.

The computational results on CsPbBr<sub>3</sub> again highlight the versatility and efficiency of the SCP theory for studying lattice dynamics in solids. While it is tempting to state that the SCP-based approaches are already reliable enough to make a quantitative prediction of structural phase transitions, many effects are yet to be investigated, including thermal expansion and choice of the exchange-correlation functionals. Investigating these effects on a  $T_c$  value would be an important future direction for our forthcoming studies.

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# Neutron Spin Resonance and Horizontal Line Nodes in Sr<sub>2</sub>RuO<sub>4</sub>

### K. Iida, K. Suzuki, and T. Masuda

 $Sr_2RuO_4$  with  $T_c = 1.5$  K has attracted a great deal of interest as the prime candidate for the chiral p-wave superconductor. Recently, however, experimental and theoretical studies under an application of uniaxial pressure along <100> reported a factor of 2.3 enhancement of T<sub>c</sub>, raising the possibility of an even-parity spin-singlet order parameter in Sr<sub>2</sub>RuO<sub>4</sub> [1]. More recently, new NMR results demonstrated that the spin susceptibility substantially drops below  $T_{\rm c}$ , ruling out the chiral-p spin-triplet superconductivity [2]. As such, these recent works turn the research on Sr<sub>2</sub>RuO<sub>4</sub> towards a fascinating new era. So far, various experimental techniques reported that the superconducting gaps of Sr<sub>2</sub>RuO<sub>4</sub> have line nodes, but the details of the line nodes, e.g. of the vertical or horizontal nature, are not uncovered yet. Since the complete information of the superconducting gaps can shed light on the symmetry of the pairing, exclusive determination of the direction of the line nodes in Sr<sub>2</sub>RuO<sub>4</sub> is highly desirable. To investigate in detail the superconducting gap, we performed the high-resolution inelastic neutron scattering (INS) measurements and random phase approximation (RPA) calculations.

Three single crystals were co-aligned with the (*HHL*) plane been horizontal to the scattering plane using the highenergy x-ray Laue diffractometer installed at ISSP. We performed INS measurements at 0.3 and 1.8 K using the disk chopper time-of-flight neutron spectrometer AMATERAS installed at J-PARC.

The most pronounced magnetic signal in the normal state of Sr<sub>2</sub>RuO<sub>4</sub> is nearly two-dimensional incommensurate (IC) magnetic fluctuations at  $\mathbf{Q}_{\text{IC}} = (0.3, 0.3, L)$  owing to the Fermi surface nesting between (or within) the quasi-one-dimensional  $\alpha$  and  $\beta$  sheets [3]. We focused on the



Fig. 1. (a) Low-energy INS intensity maps regarding the IC magnetic fluctuations in Sr<sub>2</sub>RuO<sub>4</sub> along (*H*, *H*, 0.5). (b)  $I(\hbar\omega)$  cuts at **Q** = (0.3, 0.3, 0.5) below and above  $T_c$ . (c)  $I(\mathbf{Q})$  cuts along **Q** = (*H*, *H*, 0.5) at 0.3 and 1.8 K with the energy window of 0.56 meV. (d)  $I(\mathbf{Q})$  cut along **Q** = (0.3, 0.3, *L*) at 0.3 K with the energy window of 0.56 meV.



Fig. 2. Calculated density maps of the dynamical spin susceptibility assuming the horizontal line nodes in Sr<sub>2</sub>RuO<sub>4</sub> for energy  $\hbar \omega = 2\Delta_0$ .

low-energy IC magnetic fluctuations in Sr<sub>2</sub>RuO<sub>4</sub> below and above  $T_c$  to search a spin resonance as the feedback effect from the superconducting gaps. We observed a spin resonance with energy of  $\hbar\omega_{res} = 0.56$  meV centered at a characteristic wavevector  $\mathbf{Q}_{res} = (0.3, 0.3, 0.5)$  (Figs. 1(a)–1(c)). The resonance energy corresponds well to the superconducting gap  $2\Delta = 0.56$  meV estimated by the tunneling spectroscopy. In addition, the spin resonance shows the *L* modulation with a maximum at around L = 0.5(Fig. 1(d)), indicating the three-dimensional gap structure.

To theoretically elucidate the origin of the *L* modulated intensity of the spin resonance in Sr<sub>2</sub>RuO<sub>4</sub>, RPA calculations assuming the horizontal line nodes at the superconducting gaps were also performed. Figure 2 illustrates the calculated dynamical spin susceptibilities for energy  $\hbar \omega = 2\Delta_0$ . The dynamical spin susceptibility shows the maximum at Q = (1/3, 1/3, 0.5) and (2/3, 2/3, 0.5). The superconducting gaps with the horizontal line nodes give such the feature along *L*, which is indeed observed in our INS measurements (Fig. 1(d)).

The *L* modulation of the spin resonance and our RPA calculations indicate that the superconducting gaps regarding the quasi-one-dimensional  $\alpha$  and  $\beta$  sheets at the Fermi surfaces have the horizontal line nodes [4]. These results may set a strong constraint on the pairing symmetry of Sr<sub>2</sub>RuO<sub>4</sub>.

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# Large Enhancement of Thermoelectric Efficiency Due to Pressure-Induced Lifshitz Transition in SnSe

# H. Sakai, M. Tokunaga, and Y. Uwatoko

Control of the number of Fermi pockets, i.e., electronic valleys, in conductive materials has recently attracted a great deal of attention in terms of the emerging electronics utilizing valley degrees of freedom. An important physical aspect of the valley engineering is that the emergence and annihilation of the valleys are described by a topological electronic transition known as Lifshitz transition. The Lifshitz transition is totally different from the conventional Landau-type phase transition, because it is not accompanied by any symmetry breaking. Despite many predictions of its important roles on various quantum phenomena, the experimental verification has remained challenging.

In this study [1], we have revealed a marked influence of the pressure-induced Lifshitz transition on thermoelectric efficiency in SnSe (Fig. 1(a)), which has recently become the focus of attention for its high thermoelectric performance [2]. Thermopower, which is proportional to the energy derivative of density of states, is anticipated to be an ideal probe for the Lifshitz transition. However, it has been overlooked so far owing to the lack of a model thermoelectric material, where the valley state is controllable. Here we have discovered that the band structure as well as thermoelectric performance for SnSe is highly sensitive to the external pressure by measuring the quantum oscillation of magneto-resistivity concurrently with the thermopower in a piston cylinder type high pressure cell (Fig. 2).

The obtained pressure dependence of the quantum oscillation frequencies clearly indicates that the number of the valleys increases from two to four at ~1 GPa with increasing pressure (Fig. 1(b) upper panel), as is semi-quantitatively reproduced by the first-principles calculations. At around 1.6 GPa, the four valleys are almost equivalent in size, where the thermoelectric power factor is more than 100% higher than that at ambient pressure over a wide temperature range (10–300 K) (Fig. 1(b) lower panel).

The present result demonstrates the multi-valley state is of great importance for achieving high thermoelectric performance, providing a guide for band engineering for the SnSebased thermoelectric materials. Furthermore, since atomically thin SnSe films have recently attracted much attention





-3.5 mm

Fig. 2. Setup of the thermopower and resistivity measurements under pressure.

as a new 2D material, the controllability of valley structure presented here may help for exploring their novel functions in the future electronics.

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# Cyclotron Resonance in Near Surface of InAs Quantum Well

# G. A. Khodaparast, B. A. Magill, and Y. H. Matsuda

Electronic states of semiconductor nanostructure near surface has been attracting much attention in terms of controlling quantum effects that can emerge through correlation with a superconductor. Josephson junctions made from Al-InAs have been used to create tunable superconducting qubits [1]. The key feature of the superconductor (Al) and semiconductor (InAs) nanostructure is that the two-dimensional gas (2DEG) is confined near the surface, in close proximity to the superconductor.

Although the electronic state of a bulk InAs is well understood, it is expected that the quantum confinement effect modifies the electronic state. Moreover, a narrow gap semiconductor exhibits small effective mass and large g factor, and the non-parabolicity of the band due to the confinement affects these fundamental parameters. Investigation of the electronic state of the 2DEG in InAs quantum well is essential for development of the novel semiconductorsuperconductor device. In the present study, the cyclotron resonance (CR) of an InAs quantum well has been investigated. Clear spin-split cyclotron resonance has been observed and the effective mass and the g factor are deduced as a function of magnetic field.

The CR experiment was performed with the single-turn

coil (STC) at the ISSP for magnetic field generation and an infrared CO<sub>2</sub> gas laser as the light source. The wavelengths used were 9.22, 10.48, and 10.6 µm. The laser light shines the sample and the transmitted light intensity was measured as a function of time during a pulse of a magnetic field (B)generated by the STC. A high speed HgCdTe PIN photo diode was used for detection of the light signal. The samples were grown on a semi-insulating InP (100) substrate, using a molecular beam epitaxy system. The  $In_xAl_{1-x}As$  buffer is grown at low temperature to help mitigate formation of dislocations originating from the lattice mismatch between the InP substrate and higher levels of the heterostructure [2]. The indium content of  $In_xAl_{1-x}As$  is step-graded from x = 0.52to 0.81. Next, a delta-doped Si layer of ~  $7.5 \times 10^{11}$  cm<sup>-2</sup> density is placed here followed by 6 nm of In<sub>0.81</sub>Al<sub>0.19</sub>As. The quantum well is grown next, consisting of a 4 nm thick layer of In<sub>0.81</sub>Ga<sub>0.19</sub>As layer, a 4 nm thick layer of InAs, and finally a 10 nm thick top layer of In<sub>0.81</sub>Ga<sub>0.19</sub>As.

Figure 1 shows the CR spectra at 300 and 20 K. In the upper panel, the CR peaks around 40 T indicated by solid allows are interpreted as the spin-split resonances : They are the inter-Landau level transitions between n = 0 and n = 1 with different spin polarization, where n is the Landau level index. Another CR peak at around 55 T is, on the other hand, due to the transition between n = 1 and n = 2 levels. When the temperature is lowered to 20 K, only one of the spin-split CR peaks is observed, which can be explained in terms of the population of carriers. They populate only in the lowest level at a low temperature. Remaining 55-T CR peak confirm that this resonance is due to non-equilibrium distributed carriers.

The effective mass of electrons  $(m^*)$  is directly deduced from the peak position  $B_c$ . The left-panel of Fig. 2 shows the magnetic field dependence of  $m^*$ . It is found that they are considerably larger than the band-edge effective mass of a bulk InAs  $0.023m_0$ , where  $m_0$  is the mass of a free electron. The large effective mass is due to the quantum confinement



Fig. 1. Cyclotron resonance (CR) in the InAs quantum well. The upper panel shows the resonance spectrum at 300 K. The two solid arrows suggest the spin-split CR. The broad CR indicated by the dashed arrow is due to the inter-Landau level transition between n = 1 and n = 2. The lower panel shows the CR at 20 K. Observation of only single peak near 40 T indicates effect of the thermal population of carriers. Since the CR around 55 T is considered to be due to the non-equilibrium of electrons, it remains at a low temperature.



Fig. 2. Left-side panel: The obtained effective mass of electrons. The rather large field variation indicates the strong non-parabolicity of the energy band. The right-side panel: The g-factor deduced from the experiment and numerical analysis. It is clear that g-factor is also affected by the non-parabolicity.

effect and the cyclotron energy. The enhancement of  $m^*$  with increasing magnetic field is interpreted as a result of the non-parabolicity of the band due to the cyclotron energy. The g factor can also be obtained by comparison between the CR peak position and the calculated inter-Landau level energies. It has been found that the g factor becomes small with increasing cyclotron energy. The g factor of a bulk InAs is known to be -14.

The magnetic field dependences of the  $m^*$  and g leads us to the values at zero magnetic fields and they are found to be  $0.027m_0$  and -12, respectively [3]. Determination of these quantum parameters will significantly contribute development of the novel Josephson-junction devices.

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# Many-Body String Excitations in the Antiferromagnetic Ising Spin Chain Compound BaCo<sub>2</sub>V<sub>2</sub>O<sub>8</sub>

### Z. Wang, Y. Kohama, and K. Kindo

The one-dimensional (1D) spin-1/2 Heisenberg-Ising model is the paradigmatic model for the study of quantum phase transitions and spin dynamics. However, the realization of this spin model in a solid-state material and its study are quite challenging. Several criteria must be fulfilled simultaneously: 1. the intrachain coupling should be dominant over the interchain coupling. 2. A significant Ising-like anisotropy should be present. 3. The required experimental conditions, such as high magnetic fields, should be available.

These criteria were found to be realized in the spin-1/2 Heisenberg-Ising chain antiferromagnetic material BaCo<sub>2</sub>V<sub>2</sub>O<sub>8</sub>. Our recent work has revealed a unique quantum critical behaviors under a strong transverse magnetic field  $(B\perp c)$  of 40 T [1], which is characteristic for the transversefield Ising quantum critical point. In contrast, in an applied longitudinal field (B//c), the phase diagram of the Heisenberg-Ising antiferromagnetic chain is completely different. Two phase transitions can be induced, and the different phases are characterized by different quantum spin excitations. In this work, we performed high-resolution terahertz spectroscopy and magnetocaloric-effect (MCE) measurements in BaCo<sub>2</sub>V<sub>2</sub>O<sub>8</sub> as a function of temperature and applied longitudinal magnetic field [2]. We found characteristic features revealing the field-induced quantum phase transitions, and observed the characteristic spin dynamics for the various phases. In particular, many-body string excitations as well as low-energy fractional excitations [3] were identified in the field-induced gapless phase, by comparing to the Bethe-Ansatz calculations [2]. Moreover, approaching the field-induced quantum phase transition from higher field, we observed a dominant contribution of the higher-energy string states than the lower-lying fractional excitations, in contrast to the conventional belief.

Figure 1(a) shows the MCE data, T(B), measured at different initial temperatures. The T(B) starting from 1.7 K at zero field reaches a minimum at the critical field  $(B_c)$ of 3.8 T, following by a slight increase towards higher fields. Before the temperature jump above the saturation fields of 22.9 T, the MCE detect a weak minimum at about 19.5 T. The weak minimum corresponds to the half-saturated magnetization as seen in Figure 1(b) and possibly reflects commensurate fluctuations. In down-sweeping data, the T(B) curve matches with the up-sweeping curve, except for a (irreversible) heating effect at the phase boundary. At higher temperatures, the anomalies at the critical and the half-saturated fields broaden and smear out, whereas the minimum at saturation fields remains and becomes the dominant feature. These observations qualitatively agree with the calculated phase diagram for the 1D Heisenberg-Ising



Fig. 1. (a) Magnetocaloric effect T(B), (b) magnetization of BaCo<sub>2</sub>V<sub>2</sub>O<sub>8</sub> measured in the longitudinal configuration (B//c). The solid red line in (b) is calculated from the Bethe ansatz solution of the Heisenberg-Ising model with a paramagnetic background.

model, confirming that the  $BaCo_2V_2O_8$  is a suitable system for investigating the string and the additional fractional magnetic excitations. This conclusion is also checked by the magnetization data, which shows quantitatively agreement with the 1D Heisenberg-Ising model (Red curve in Fig.1(b)).

We investigated the dynamical properties with THz transmission spectra in the applied longitudinal magnetic field. These data are available in Ref. [2] which tracked the field dependence of exotic spin excitations, i.e., many-body string and fractional excitations. We have revealed their selection rule in the vicinity of a field induced QCP in the Ising-like spin-1/2 chain compound. While the gapped fractional excitations are dominant in the 3D ordered state, we found that the high-energy string excitations plays an important role in quantum critical dynamics, which is consistent with Bethe-Ansatz calculations [2].

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# **Operando** Soft X-ray Emission Spectrosopy of Fe<sub>2</sub>O<sub>3</sub> Anode for Li-Ion Battery

### D. Asakura, E. Hosono, J. Miyawaki, and Y. Harada

Improving the energy and power density of electrode materials for Li-ion batteries (LIBs) is highly important to further develop electric vehicles. For the improvements of battery performance, understanding the charge (Li-extraction) and discharge (Li-insertion) mechanisms from the viewpoint of the electronic structure is indispensable. Here, we demonstrate operando Fe L3-edge resonant XES for Fe<sub>2</sub>O<sub>3</sub> which is an anode material of LIB [1]. It is known that the discharge/charge mechanism is based on conversion reaction denoted as  $Fe_2O_3 + 6Li^+ + 6e^ \Leftrightarrow$  3Li<sub>2</sub>O + 2Fe [2,3]. To confirm the conversion reaction and further investigate the electronic-structure charge, we analyzed the operando XES spectra using full-multiplet calculation [4,5].

The operando cell consists of Fe<sub>2</sub>O<sub>3</sub> poly-crystalline thin film (~100 nm), a Li-metal counter electrode, and an electrolyte solution [1,6]. The operando XES experiments were carried out with the HORNET XES spectrometer at BL07LSU of SPring-8 [7]. The electrochemical discharge/charge was performed by cyclic voltammetry. The operando XES measurements were at an open-circuit voltage (OCV), discharged state and charged state on the second discharge-charge cycle.

Figure 1 shows the XES results [1]. The XES spectrum for the initial state is attributed to Fe<sup>3+</sup> state because the XES line shape is almost the same as that for Fe<sub>2</sub>O<sub>3</sub> in previous reports [8]. On the other hand, the valence of Fe at the OCV before the second cycle was not  $Fe^{3+}$ , but  $Fe^{2+}$  with a weak p-d hybridization, suggesting considerable irreversibility on the first discharge-charge cycle and a weakened Fe-O bond after the first cycle. Moreover, we revealed that



Fig. 1. Operando Fe L<sub>3</sub>-edge resonant XES spectra for the Fe<sub>2</sub>O<sub>3</sub> on the second cycle taken with the excitation energy  $E_{in} = 708.2 \text{ eV}$  [1]. The Fe  $L_3$ -edge XES spectrum for the initial state is also displayed. All the spectra are plotted as a function of energy loss ( $E_{loss}$ ).

the Fe 3d electronic-structure change during the second cycle was to some extent reversible as  $Fe^{2+}$  (2.7 V vs. Li/Li<sup>+</sup>: OCV)  $\rightarrow$  Fe<sup>0</sup> (0.1 V vs. Li/Li<sup>+</sup>: discharged)  $\rightarrow$  Fe<sup>(2+d)+</sup> (3.0 V vs. Li/Li<sup>+</sup>: charged). This operando Fe L3-edge resonant XES in combination with the full-multiplet calculation provides detailed information for redox chemistry during a discharge-charge operation that cannot be obtained by other methods such as crystal-structure and morphology analyses. XES is thus very powerful to investigate the origin and limitation of the lithiation function of anodes involving conversion reaction.

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# Mass Transport in the PdCu Phase Structures during Hydrogen Adsorption and **Absorption Studied by Ambient-Pressure** XPS under Hydrogen Atmosphere

### J. Tang, I. Matsuda, and J. Yoshinobu

Pd-based alloys have been the attractive materials for the hydrogen permeation process, because they possess higher hydrogen permeability and suppress the hydrogen embrittlement compared to pure Pd bulk. It was reported that the PdCu alloy, especially so-called "PdCu40 alloy", has a relatively higher hydrogen diffusivity than the other Pd-alloys (PdAg, PdAu, PdRh, etc.). Industrial usages of the  $PdCu_{40}$  alloys with the high Cu content also improve the economic perspectives because of the lower Cu cost. Although there are advantages of PdCu alloys in the application fields, it requires further improvements in microscopic aspects. For example, hydrogen solubility of the facecentered cubic (fcc) structure of a PdCu alloy is approximately one order of magnitude higher than that of bodycentered cubic (bcc) structure.

In the present research, we traced Pd and Cu atoms during hydrogen adsorption and absorption processes at the elemental steps, dissociative adsorption of H atoms on the surface and dissolution of H atoms into the bulk, by the individual core-level photoelectron spectroscopies under the hydrogen atmosphere [1]. The absorption process is investigated by the Ambient Pressure (AP)-XPS measurements at the soft X-ray undulator beamline BL07LSU at SPring-8. The PdCu<sub>40</sub> sample, provided from Tanaka Kikinzoku Kogyo K.K., was annealed at 673 K to form the B2 phase structure. Then, the B2/fcc phase structure was prepared by subsequent annealing at 1000 K. Figures 1(a) and (b) show the



Fig. 1. XRD patterns of (a) B2 and (b) fcc/B2 mixed-phase PdCu alloys.



Fig. 2. Pd  $3d_{5/2}$  spectra measured on (a) clean surface, and under H<sub>2</sub> exposure at 1.5 Torr at (b) 300 K, (c) 373 K, (d) 473 K, (e) 573 K with photon energy of 680 eV on PdCu(B2) alloy. Pd  $3d_{5/2}$  spectra measured on (f) clean surface, and under H<sub>2</sub> exposure at 1.5 Torr at (g) 300 K, (h) 373 K, (i) 473 K, (j) 573 K with photon energy of 680 eV on PdCu(fcc/ B2) alloy. Surface Pd component, bulk Pd component, CO adsorption component and Pd-H component are presented with green, blue, purple, and yellow solid lines, respectively.

XRD patterns of the B2- and fcc/bcc- phased PdCu alloys, respectively. Figures 2 and 3 show the temperature dependence of hydrogen absorption reactions on the B2 and fcc/ bcc phases, observed by measuring the Pd  $3d_{5/2}$  and Cu  $2p_{3/2}$  XPS spectra during the hydrogen exposure at 1.5 Torr at 300-573 K. The temperature-dependent data show that a number of the Pd-H bond increased accompanied with the decrease of the Cu-H bond with temperature. The Pd hydride formation in the B2 and fcc/bcc structures show the same behavior at 300-373 K, however, more Pd hydride was formed in the B2 structure than in the fcc/bcc structure at 473-573 K. The decrease rate of Cu-H component is higher in the B2 phase than fcc/bcc phase. These results indicate that the interstitial hydrogen occupied the different sites in the PdCu alloy bulk at different temperature and confirms the difference in absorption between the two phases. Comparing with the previous calculation [2], the significant enhancement of the hydride formation at 473 K can consistently be described in terms of variation of the hydrogen diffusion paths from the Cu-rich octahedral site to the energetically favorable Pd-rich octahedral site. Furthermore, the activation energy of the hydrogen diffusion is found to be lower in the B2 phase than that in the fcc/B2 phase. Our elucidation of hydrogen diffusion mechanisms on the different phase structures gives a new understanding of the hydrogen absorption process, which could be the critical point for the rate-limiting process in the hydrogen permeation through the PdCu alloy.

Similar investigation on hydrogen permeation process was carried out for the PdAg alloy[3]. The measurements of AP-XPS revealed that Pd atoms were also found to reactive sites during hydrogen absorption. On the other hand, the process is likely promoted by the Pb segregation. It is of interest to make systematic investigations of individual Pd-alloys to capture the whole picture.

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# Sub-Cycle Spectroscopy of Proton Transfer in Ferroelectric Cocrystals Driven by Intense THz and MIR Fields

### T. Umanodan, Y. Okimoto, and J. Itatani

Ferroelectricity in organic materials is one of the most important topics in condensed matter physics. It has a wide range of practical applications because organic systems possess advantages such as mechanical flexibility, printability, disposability, and cost-effectiveness. Very recently, proton-mediated co-crystals have been developed as novel organic ferroelectric materials [1]. In these co-crystals, proton ordering along the hydrogen bonds between the proton-donor and -acceptor molecules leads to the emergence of ferroelectricity, leading to the lack of inversion symmetry. We focused on a proton-mediated co-crystal [H-dppz][Hca] (dppz = 2,3-di(2-pyridinyl)pyrazine, Hca = chloranilate) that



Fig. 1. (a) Crystal structure of Hdppz-Hca cocrystal. (b, c) Schematic illustrations of the (b) ferroelectric and (c) paraelectric phases.

shows ferroelectricity at room temperature ( $T_c = 402$  K). Figure 1 shows the crystal structure (a), the ferroelectric and paraelectric origins due to the position of protons (b, c), and the imaginary part of dielectric constant at room temperature (d).

In this study [2], we investigated the ultrafast dielectric response of [H-dppz][Hca] by sub-cycle spectroscopy where carrier-envelope phase-stable intense optical pulses at 1 or 40 THz drove the ferroelectricity, then sub-cycle visible pulses probes the field-driven dynamics.

First, we irradiated the co-crystal with a single-cycle THz pulse at a center frequency around 1 THz with a maximum electric field of ~1 MV/cm, and measured the second harmonic (SH) of 100-fs laser pulses at 800 nm as a function of the relative delay between the THz and 800-nm pulses. The modulation of SH intensity exactly followed the waveform of the applied THz electric field, and the magnitude of the relative SH change reached up to 10%. This result indicates that the ultrafast change of the ferroelectricity was directly driven by the THz electric field.

Second, we irradiated the crystal with an intense mid-infrared (MIR) pulse (center frequency ~40 THz, maximum electric field ~30 MV/cm), and found that the induced SH change occurred very differently. The time profile of observed change of SH intensity was not scaled by the field profile of the 40 THz pulse as shown in Fig. 2(b). The SH change contained a component proportional to the square of the applied electric field in addition to the linear component that is proportional to the field as observed in the 1-THz case. These results suggest that the change of the polarity of the co-crystal cannot follow the oscillation of the electric field at 40 THz.

To understand these field effects, we analyzed the following nonlinear equation of motion that contains the C-O<sup>-</sup> stretching mode,

$$\mu \frac{d^2 X(t)}{dt^2} + \mu \gamma \frac{dX(t)}{dt} + \mu \Omega^2 X(t) + a \mu X^2(t) = a E_{MIR}(t),$$

where  $\chi(t)$  is the change in amplitude of the normal mode, which can be viewed as an index of the displacement of the atoms including the protons caused by the intense MIR electric field  $E_{MIR}(t)$ . We used the experimental data for  $E_{MIR}(t)$  that was obtained by EO sampling with 6-fs visible pulses. The values  $\mu$ ,  $\Omega$ , q, are the reduced mass, frequency, and effective charges of the C-O- mode derived from a DFT calculation and reflectivity data. We fit the observed time profile of  $\Delta I_{SH}/I_{SH}$  by numerically solving the above



Fig. 2. (a-d) Calculated amplitudes of C-O<sup>-</sup> stretching mode for various anharmonic parameter a. The black circles in (c) denote the observed time profile of the SH intensity. (e, f) Schematic illustrations of the proton motion in the binding potential of the cocrystal when a THz or MIR pulse is applied.  $X_0$ , X' denote the equilibrium position and a metastable position with excitation pulses, respectively.

equation, and found that the observed signal  $\Delta I_{SH}/I_{SH}$  were well reproduced when  $a \approx -18$  Å<sup>-1</sup>fs<sup>-2</sup>,  $\gamma \approx 0.75$  eV, and  $k \approx$ 26  $Å^{-1}$  as shown by the solid line in Fig. 2. This result reveals the importance of phonon excitation in our observation of unconventional positive shift of  $\Delta I_{SH}/I_{SH}$ .

Figures 2(e, f) summarize the origins of the observed SH changes for THz and MIR excitation. In the presence of a strong MIR field that resonantly excites the C-O<sup>-</sup> stretching mode, dynamical repositioning of protons occurs, which leads to the asymmetric polarization. These results can be viewed as an example of ultrafast control of organic ferroelectric cocrystals using intense ultrafast laser pulses at room temperature.

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