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研究成果の概要（和文）：本研究で着目した物質は、簡単な化学組成を有する絶縁体で、トポロジカル絶縁体の候補物質やドーピングによって非従来型の超伝導が発現する可能性を有するものである。他の様々な系に加えて、ドープされたトポロジカル絶縁体Bi2Se3 や SnTeにおける超伝導を調べ、さらに超伝導の他にも異なる興味深い特性を見出した。ドープしたWSe2では、800 Kにおいて0.35 という比較的大きな熱電性能指数を実現し、また、ドーピングによってバンド構造の変化を見出した。極性を有する(Ge,Mn)Te系においては、過去には報告されていなかった強磁性相も発見し、磁気的相変化メモリ機能の実証に成功した。

研究成果の概要（英文）：This research project focussed on chemically simple semiconducting and insulating systems, which were thought to be candidate materials for topological insulators or possess a complicated band structure, strong spin-orbit coupling, a noncentrosymmetric structure a.s.o. where possibly unconventional superconductivity might be introduced by doping. The superconductivity in the doped topological insulators Bi2Se3 and SnTe was probed as well as various more systems. Beside superconductivity, also different interesting effects were found: In doped WSe2 a comparably large thermodynamic Figure of Merit of ~0.35 at 800 K was found along with an unexpected change in the band structure from three- to two-dimensional. In the polar system (Ge,Mn)Te, an additional ferromagnetic phase was identified which had been overlooked in the past. Moreover, it was successfully demonstrated, that (Ge,Mn)Te bears magnetic phase change memory functionality.

研究分野： condensed matter physics

キーワード： Topological Insulators　Topological SC　Unconventional SC　Semiconductors　Polar distortion

１．研究開始当初の背景

Superconductivity in semiconductors with possibly low charge carrier concentration was predicted to exist in the 1960s when also the first examples were found experimentally. In recent years insulating and semiconducting systems attracted again much attention due to the prediction and experimentally finding of so-called topological insulators. Soon after the possibility of unconventional topological superconductivity was discussed. The latter is characterized by a full energy gap in the bulk and the existence of gapless Andreev-bound states hosting so-called Majorana fermions, intriguing particles, which are their own antiparticles. At the time of writing the application for this project, it was strongly called for to identify possible topological superconductor systems. The aim of this project was to find such materials by doping into topological insulators and related systems and see whether unconventional superconductivity can be induced. A prime candidate material was already identified (Cu-intercalated Bi_2Se_3; the mother compound was earlier identified as a topological insulator). Other related systems also came into the focus of research and this project as, e.g., $Sn_{1-x}In_xTe$ and $Pb_{0.77}Sn_{0.23}Se$.

２．研究の目的

Doping into low charge carrier semiconducting or insulating systems was found to be a promising gateway to unconventional or even topological superconductivity. Hence the aim of this project was to search for new superconductors by doping into semiconducting and insulating systems with potentially high impact on the topical research activities on unconventional and topological superconductivity.

Many of these systems originate from chemically simple binary compounds of the form AB, A_2B_3, a.s.o., which may bear potential for interesting physical effects, e.g., due to their often complicated band structure in spite of the chemical simplicity. Among these systems (i) materials consisting of heavy elements, where unconventional effects are expected not to be negligible, (ii) materials, which exhibit even undoped criterions for unconventional superconductivity such as noncentrosymmetry, polarity, and (iii) materials which were already identified to be topological were the natural playgrounds of this project. The possible benefit of finding new superconductors was expected not only to be of interest for fundamental research but also in terms of a possible applicability in the (not-to-near) future in the case of topological superconductivity, which is considered to have implications on topological quantum computing.

３．研究の方法

(1) Material synthesis of doped binary noncentrosymmetric, polar, and topological insulator- and topological crystalline insulator-based systems
(2) Material analysis by means of x-ray diffractometry, Laue camera, ICP and SEM-EDX analyzers
(3) Material characterization by means of electrical-transport (resistivity, Hall effect), thermal-transport (thermal conductivity, thermopower, thermal diffusivity), magnetization, and specific-heat measurements.
(4) Depending on the outcome specialized experiments (collaborations).

４．研究成果

(1) Cu-intercalated Bi_2Se_3

The above-mentioned work on $Cu_xBi_2Se_3$ had already started before this project was accepted. On this material several collaborations were continued.

One successful collaboration was an optical spectroscopy study on this system. Beside the emergence of superconductivity, the introduction of Cu was reported to lead to unusual features in transport and magnetization measurements. Here, it was found that progressive Cu doping leads to an increase of the conduction band effective mass while the charge carrier concentration remains almost constant for $x > 0.12$. It was also shown that the unusual doping dependence, i.e., suppression, of the superfluid density, as reported earlier by the present author, is mainly due to the enhancement of the effective mass rather then disorder. This is another indication that the nature of the Cu^{1+} intercalation into Bi_2Se_3 is nontrivial and hints to a complicated defect chemistry in this system, see Ref. 4.

Another important collaboration on this system were ^{77}Se-NMR (nuclear magnetic resonance) experiments. It was found that the spin-rotation symmetry is spontaneously broken in the hexagonal plane of $Cu_xBi_2Se_3$ in the superconducting state. This is expected for spin-triplet pairing but conclusive experimental evidence had not been obtained in any system yet. Hence this result does not only support the still debated unconventional spin-triplet scenario for $Cu_xBi_2Se_3$ but is also the first clear experimental finding of a broken spin-rotation symmetry in a superconductor (accepted for publication in Nat. Phys.).

(2) In-doped SnTe

SnTe is a self-doped superconductor with rather low transition temperatures T_c and which exhibits a ferroelectric distortion below approx. 100 K, i.e., it is a noncentrosymmetric system. It had been known that In-doping into SnTe enhances T_c. The finding that SnTe-based compounds exhibit a so-called topological crystalline insulating phase raised the question, whether the known superconducting phase in $Sn_{1-x}In_xTe$ might be unconventional.

In a systematic study on various differently doped single crystals, it was found that the dependence of T_c on the In-doping concentration x undergoes a qualitative change across the critical concentration $x_c \approx 0.038$ (or in terms of charge carrier concentration $p_c \approx 4.8 \times 10^{20}$ cm^{-3}), where the In content is sufficient to suppress the ferroelectric distortion and the system exhibits a doping-induced structural phase transition. Below x_c, T_c is strongly enhanced with disorder, i.e., impurity scattering, and has no correlation with x and p, while above x_c the critical temperature increases linearly with x and p, see Fig. 1. Interestingly and very unusually, the highest values of T_c were found in samples which exhibit the largest degree of disorder as quantified by the residual resistivity. Specific-heat measurements confirmed that the superconductivity is a bulk feature in these samples. The specific-heat data can be reasonably well-described by the BCS theory, which implies a nearly isotropic gap magnitude. However, there are some indications which allow to speculate that in $Sn_{1-x}In_xTe$ conventional even- and unconventional odd-parity pairing states are competing. Given the unusual dependence of T_c on the impurity scattering, in the highest T_c samples the odd-parity states might be suppressed by non-magnetic impurity scattering and they can only survive in samples with low T_c values and small impurity scattering, see Ref. 5.

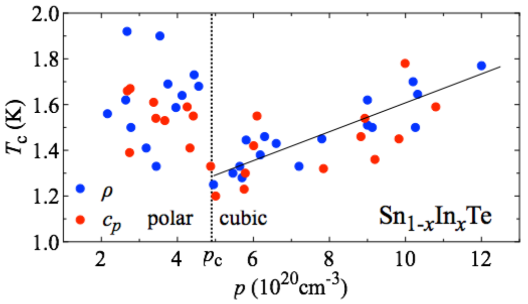

Fig. 1. T_c vs p plot of superconducting $Sn_{1-x}In_xTe$, see text.

(3) $A_x(Pb_{0.77}Sn_{0.23})_{1-x}Se$

$Pb_{0.77}Sn_{0.23}Se$ was reported to be a topological crystalline insulator, which was the motivation to try to induce (possibly topological) superconductivity in this system by doping, similar to the case of Cu-intercalation into Bi2Se3. Beside the "pure" system, which was also checked for superconductivity down to approx. 300 mK, the following elements were doped: A = Ag, Bi, Ca, Cu, Fe, In, La, Pb, and Tl. Unfortunately no bulk superconducting composition was found. In the case of Tl doping traces of a superconducting transition were found in a certain doping range, but it turned out that they were due to a minority phase and not a bulk effect.

(4) Doped WSe_2

WSe_2 belongs to a class of materials in which a rich variety of physical properties is observed, as, e.g., charge-density wave order, superconductivity, or thermoelectrical device functionality. As in SnTe, a complicated band structure consisting of many valleys is at least related to or responsible for the features observed in these compounds.

Here several elements were doped into the insulator WSe_2 on both the W and the Se side. It was known that, e.g., Ta can be easily incorporated into WSe_2 and leads to p-type (hole) conductivity and a comparably low thermal conductivity. The latter was reported to be responsible for thermoelectrical Figure-of-Merit values up to 0.6 around 800 K. Here the initial motivation was to make the system n-type, i.e., induce electrons as charge carriers by Re, Cr, Mn, and Cu doping (stoichiometrical and excess). Unfortunately all attempts to induce

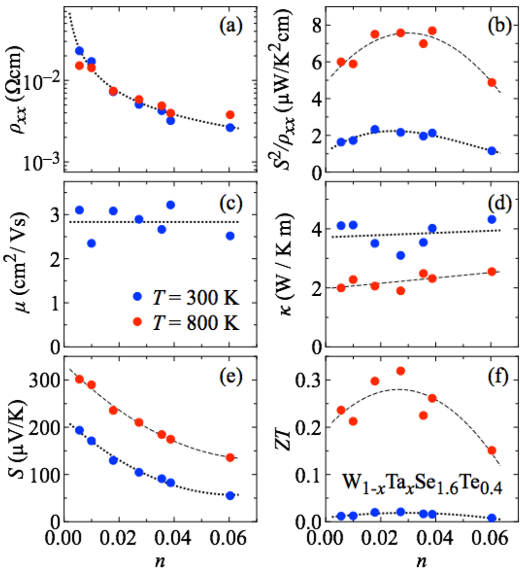

Fig. 2. Summary of transport data of codoped $W_{1-x}Ta_xSe_{1.6}Te_{0.4}$, see text.

n-type conduction failed. In a next step, Se was substituted by Te and S and (hole) charge carriers were induced by Ta codoping on the W side. It was found that the additional disorder induced by the Te doping further reduces the thermal conductivity. However, this merit is overcompensated by an increased resistivity due to the additional disorder induced into the anion sublattice and therefore an increased scattering rate for the p-type charge carriers. Hence the observed maximum Figure of Merit was reduced to approx. 0.3 at 800 K as compared to the case without codoping at the Se side, see Fig. 2.

Another interesting effect due to the Te codoping into $W_{1-x}Ta_xSe_{1.6}Te_{0.4}$, which was observed, is a change in the band structure. The isotropic band at the Γ point of the hexagonal Brillouin zone of WSe_2 is lowered in energy while the bands at the K and K’ points shift towards the Fermi level upon successive Te doping. The band structure at the K and K’ points is of anisotropic nature. This leads to a change of the character of the doped charge carriers (by Ta), i.e., it changes from filling solely into isotropic bands to filling into bands of both isotropic and anisotropic character. This crossover was successfully monitored in the electronic specific-heat coefficient as estimated from heat-capacity measurements. This observation is in qualitative agreement with band structure calculations carried out in collaboration with theorists. Interestingly, this shift of the valence band maximum is reminiscent of the situation in noncentrosymmetric monolayer dichalcogenides, which recently attract much interest due to the finding of valley-spin coupling and electric-field induced superconductivity in electric double-layer transistors, see Ref. 3.

(5) Mn-doped GeTe

The situation of GeTe is qualitatively similar to that of SnTe with the exception that this system is not considered to be topological. There is also a ferroelectric distortion, which in GeTe sets in at much higher temperatures well above room temperature. As SnTe, at low temperatures GeTe is a noncentrosymmetric self-doped superconductor. In contrast to SnTe, it exhibits in addition a giant Rashba spin splitting. It was known that Mn-doping into GeTe induces ferromagnetic order which was explained in an RKKY-type framework. The motivation here was the question, how dilute Mn doping, i.e., the introduction of magnetism, acts on the Rashba spin-split band structure and if the superconductivity survives doping with magnetic ions, which is expected to produce unconventional effects. However, during this study a completely different feature was found. It turned out that there are two distinct competing magnetic phases for low Mn concentrations as indicated by very different onset temperatures T_c of ferromagnetism. The low-T_c phase exhibits a linear increase of T_c with x while the high-T_c phase features a dome-like phase line in the magnetic phase diagram, see Fig. 4. The latter had not been reported in literature and hence was completely overlooked in the past. At around x = 0.05 the difference in T_c between the two phases is as large as a factor of five to six. Interestingly this difference disappears when the system becomes cubic upon progressive Mn doping. (The rhombohedral distortion is reduced and above approx. x = 0.12 the high-temperature cubic phase is stable down to low temperatures.) What magnetic phase is realized was found to depend on the heat treatment of a sample. When quenching a sample from the high-temperature cubic phase into water, the low-T_c phase is formed, while cooling a sample slowly and controlled down to room temperature leads to the formation of the high-T_c phase. Moreover it was found that switching between the two phases back and forth is repeatedly possible. This demonstrates that (Ge,Mn)Te is a magnetic analog to the well-known structural

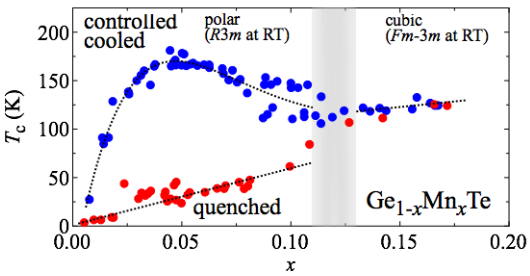

Fig. 3. Magnetic phase diagram of Mn-doped GeTe, see text.

phase-change materials, where the structure of a sample is locally switched between amorphous and crystalline states. Hence magnetic phase-change memory functionality was successfully demonstrated. This is conceptually different from memory devices employing structural effects: Here no (re-) crystallization process is involved.

The underlying mechanism is probably a spinodal decomposition in the low-Mn-concentration region of the phase diagram upon slow cooling. The system exhibits an instability agains composition fluctuations leading to a quasi-periodic modulation of the Mn concentration, i.e., there are Mn-rich and -poor regions formed in a sample. In the present case, the low-T_c phase is much more homogeneous in terms of Mn distribution (and hence less distorted), while the high-T_c phase consists of Mn-rich islands in a lake of Mn-poor, almost pristine and more strongly distorted GeTe. This scenario is consistent with results of high-resolution synchrotron XRD measurements carried out on various quenched and slowly-cooled samples, where the nanoscale spinodal decomposition can be traced in terms of line-broadening. Also, the different degrees of inhomogeneity were successfully visualized by EDX images, see Ref. 1.

５．主な発表論文等

（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計 7 件）

(1) Heat-Treatment-Induced Switching of Magnetic States in the Doped Polar Semiconductor $Ge_{1-x}Mn_xTe$
M. Kriener, et al. (10 authors), Sci. Rep. 6, 25748 (2016), (peer reviewed),
doi:10.1038/srep25748

(2) Magnetoelectric effect and magnetic phase diagram of a polar ferrimagnet $CaBaFe_4O_7$
V. Kocsis, Y. Tokunaga, S. Bordács, M. Kriener, A. Puri, U. Zeitler, Y. Taguchi, Y. Tokura, and I Kézsmárki,
Phys. Rev. B 93, 014444 (2016),
(peer reviewed)
doi:10.1103/PhysRevB.93.014444

(3) Modification of electronic structure and thermoelectric properties of hole-doped tungsten dichalcogenides
M. Kriener, A. Kikkawa, T. Suzuki, R. Akashi, R. Arita, Y. Tokura, and Y. Taguchi
Phys. Rev. B 91, 075205 (2015),
(peer reviewed)
doi:10.1103/PhysRevB.91.075205

(4) Doping-dependent charge dynamics in $Cu_xBi_2Se_3$
L. J. Sandilands, A. A. Reijnders, M. Kriener, K. Segawa, S. Sasaki, Y. Ando, and K. S. Burch
Phys. Rev. B 90, 094503 (2014)
(peer reviewed)
doi:10.1103/PhysRevB.90.094503

(5) Unusual nature of the fully-gapped superconductivity in In-doped SnTe
M. Novak, S. Sasaki, M. Kriener, K. Segawa, and Y. Ando
Phys. Rev. B 88, 140502 (2013)
(peer reviewed)
doi:10.1103/PhysRevB.88.140502

(6) Experimental studies of the topological superconductor $Cu_xBi_2Se_3$
Y. Ando, K. Segawa, S. Sasaki, and M. Kriener
J. Phys.: Conf. Ser. 449, 012033 (2013)
(peer reviewed)
doi:10.1088/1742-6596/449/1/012033

(7) Anomalous Dressing of Dirac Fermions in the Topological Surface State of Bi_2Se_3, Bi_2Te_3, and Cu-Doped Bi_2Se_3
T. Kondo, Y. Nakashima, Y. Ota, Y. Ishida, W. Malaeb, K. Okazaki, S. Shin, M. Kriener, S. Sasaki, K. Segawa, and Y. Ando
Phys. Rev. Lett. 110, 217601 (2013)
(peer reviewed)
doi:10.1103/PhysRevLett.110.217601
This paper is an Editors' Suggestion.

〔学会発表〕（計 15 件）

(1) Magnetic Phase Diagram of the Doped Polar Semiconductor GeTe,
M. Kriener, 2016/03/28,
Indo-Japan Conference on Emergent Phenomena in Transition-Metal Compounds and Related Materials,
Indian Institute of Science, Bengaluru (Bangalore), India (Invited Talk)

(2) Origin of the Enhancement of the Ferromagnetic T_c in $Ge_{1-x}Mn_xTe$ by Structural Analysis, M. Kriener, 2016/03/21, 71st Spring Meeting of the Physical Society of Japan, Tohoku Gakuin University, Sendai, Japan (Contributed Talk)

(3) Enhanced Ferromagnetism due to Nanoscale Phase Separation in the Polar Ferromagnet (Ge,Mn)Te, M. Kriener, 2015/10/31, 3rd CEMS Topical Research Camp, Hotel Kinugawagyoen, Kinugawa, Japan (Contributed Talk)

(4) Magnetic Phase Diagram of the Polar Semiconductor $Ge_{1-x}Mn_xTe$, M. Kriener, 2015/09/18, JPS Autumn Meeting, Kansai University, Suita, Japan (Contributed Talk)

(5) Competing Magnetic Phases in the Doped Polar Semiconductor GeTe, M. Kriener, 2015/07/15, Institute of Physics II, University of Cologne, Cologne, Germany (Invited Talk)

(6) The Magnetic Phase Diagram of Mn-Doped GeTe Crystals, M. Kriener, 2015/07/10, International Conference on Magnetism 2015, Barcelona, Spain (Poster Presentation)

(7) Different Magnetic Phases in the Doped Polar Semiconductor GeTe, M. Kriener, 2015/07/03, Institute of Condensed Matter Physics, EPF Lausanne, Lausanne, Switzerland (Invited Talk)

(8) Competition of the Magnetic Phases in the Doped Polar Semiconductor GeTe, M. Kriener, 2015/07/02, Institute for Theoretical Physics, ETH Zürich, Zürich, Switzerland, (Invited Talk)

(9) Competing Magnetic Phases in a Diluted Magnetic Semiconductor, M. Kriener, 2015/06/01, RIKEN-AIST Workshop, RIKEN, Wako, Japan (Poster Presentation)

(10) Competing Magnetic Phases in the Polar Magnetic Semiconductor GeTe, M. Kriener, 2015/05/26, Workshop on Topological Magnets, RIKEN, Wako, Japan (Poster Presentation)

(11) Doping-Induced Ferromagnetism in the Polar Semiconductor GeTe, M. Kriener, 2014/10/09, 2nd CEMS Research Camp, Hotel Matsunoi, Minakami, Japan (Contributed Talk)

(12) Doping Effect on the Thermoelectric Properties of $WSe_{1.6}Te_{0.4}$, M. Kriener, 2014/09/07, 69th Autumn Meeting of the Physical Society of Japan, Chubu University, Kasugai, Japan (Contributed Talk)

(13) Thermoelectric Properties of $W_{1-x}Ta_xSe_{1.6}Te_{0.4}$, M. Kriener, 2014/07/17, 1st CEMS Topical Research Camp, Hotel Heartpia, Atami, Japan (Contributed Talk)

(14) Possible Topological Superconductivity in $Cu_xBi_2Se_3$ and $Sn_{1-x}In_xTe$, M. Kriener, 2014/03/18, The 3rd Super-PIRE REIMEI Workshop on Frontiers of Condensed Matter Physics, Institute of Physics, Beijing, China (Invited Talk)

(15) Thermoelectrical Properties of $(WTa)(SeTe)_2$, M. Kriener, 2013/11/14, FIRST-QS^2C Workshop on Emergent Phenomena of Correlated Materials, Shinagawa Intercity Hall, Tokyo, Japan (Poster Presentation)

〔産業財産権〕
○出願状況（計１件）
名称：メモリデバイス及び情報処理装置
発明者：Y. Taguchi, M. Kriener, Y. Kaneko, and Y. Tokura
権利者：国立研究開発法人理化学研究所
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国内外の別： Japan

〔その他〕
Coworkers and me received 2013 the “17th Superconductivity Science and Technology Award” from the Forum of Superconductivity Science and Technology, Japan.

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