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研究成果の概要（和文）：複雑なバンド構造は、トポロジカル電子相、超伝導、熱電性能、また特異なスピン構造など、様々な興味深い物性を誘発する。本研究では、トポロジカルな電子相と超伝導との相関の解明。実験では、SnTe、GeTe、Cd3As2などの候補物質に系統的なキャリアドープを行なった。SnTeとGeTeにおいては超伝導の発現を確認し、特に後者は世界初の成果となった。その起因は原子価不安定性にあると考えられるが、これは現在、超伝導相互作用増強の起源として議論が進んでいる。トポロジカルな電子状態で話題となっているなCd3As2においても、ドーピングによる物性制御が可能であることが明らかとなった。

研究成果の学術的意義や社会的意義
本研究では、超伝導と相互作用するトポロジカル電子相を検出することを目的とした。電子物性におけるトポロジーは、約15年前に始まった固体物理学の比較的新しい概念であり、関連した物性は当初、低温/強磁場のような特殊な環境でのみ発現すると考えられていた。本研究によって、多くの物質が様々な環境において、超伝導を含むトポロジカルな物性を発現しうることが明らかとなり、将来的な量子計算機等への応用につながる知見が得られたと考えられる。

研究成果の概要（英文）：Solids exhibiting a complicated band structure (i.e., their peculiar electronic nature) host various interesting physical phenomena, such as topological phases of matter, superconductivity, thermoelectric properties, or complicated spin structures. To identify, understand, and eventually exploit such features are key targets of research in solid state physics. Here the focus was lying on topological features combined with superconductivity. The approach was to dope into promising starting materials, such as SnTe, GeTe, Cd3As2, and others. Superconductivity in SnTe and GeTe (in the latter it was discovered for the first time) and its relationship to valence instabilities was explored. Such valence instabilities are discussed as a possible origin of enhanced superconducting interactions. Cd3As2, famous for its unconventional so-called "topological" nature, was also explored. By doping, a fine control was achieved over its interesting features.

研究分野： Condensed Matter Physics

キーワード： Topol. Superconductivity　Topological Insulators　Polar Semiconductors　Weyl Semimetals　Electronic structure　valence-skipping

1．研究開始当初の背景

In the past 15 years so-called topological nontrivial systems attracted a huge interest in the solid-state physics community, and a new research field got established. The wave functions of quantum states in topological systems are characterized by invariants protected by certain symmetries, such as time-reversal symmetry. Practically topological insulators exhibit conducting (gapless) surface states while the bulk is insulating. Soon after the discovery of such topological systems, the hunt for a superconducting analog started: topological superconductors. Thanks to their nontrivial topology, it is expected that so-called Majorana fermions, particles which are their own antiparticles, form at the surface of such compounds. These are thought to bear potential for fault-free quantum computing in the far future. Meanwhile additional topological invariants were discovered and theoretically described, namely Dirac and Weyl semimetals where rich and comprehensive new physics is expected and predicted to be realized.

2．研究の目的

The aim of this project was to probe existing / theoretically discussed topologically nontrivial systems and possibly discover new ones not only but also with emphasis on superconductivity. This would allow a better understanding of the underlying physics and is expected to help to pave the way towards future applications. Beside topologically nontrivial systems, during the progression of this project, also some interesting superconducting systems came into focus and were examined which turned out to be topologically trivial.

3．研究の方法

(1) Material synthesis by sophisticated growth techniques of chalcogenide and arsenic systems
(2) Material characterization by means of x-ray diffractometry, inductively-coupled plasma atomic emission spectroscopy, and scanning-electron microscopy equipped with an energy-dispersive x-ray analyzer
(3) Analysis of materials' physical properties 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 of the initial characterisation and more in-depth analysis by transport and thermodynamic measurements, initiate collaborations to allow for additional more specialized experiments wherever indicated.

4．研究成果

(1) Tailoring superconductivity in SnTe

The superconducting phase in $Sn_{1-x}In_xTe$ is a long known feature which in recent years regained interest because the starting compound SnTe was theoretically predicted and soon after experimentally found to be topologically nontrivial, a so-called topological crystalline insulator. Even topological superconductivity is controversially discussed in literature at low In-doping levels around $x \approx 0.04$. However, it was unknown how the superconducting phase diagram evolves at higher doping levels since the systems undergoes a doping-induced structural phase transition around $x = 0.45$ destroying the superconductivity and hence preventing further research. Here, this drawback was overcome by employing a sophisticated sample preparation method at high pressure (about 5 GPa) and elevated temperatures (about 1000°C) motivated by an old study on pure InTe. This allowed us to synthesise the whole solid solution and reveal that the

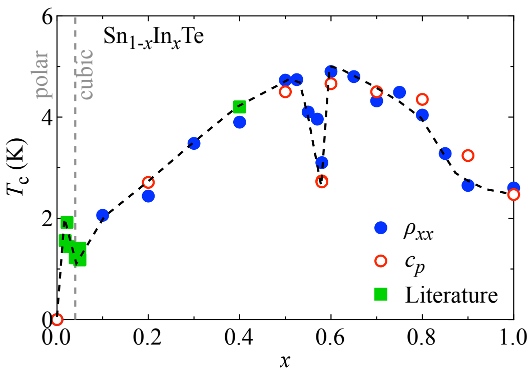

Fig. 1: Superconducting phase diagram of $Sn_{1-x}In_xTe$, see text.

superconducting phase diagram exhibits an unexpected two-dome structure with a strong and sharp suppression of the superconductivity at x = 0.58, see Fig. 1.
Although the observed superconductivity in $Sn_{1-x}In_xTe$ at higher doping concentrations is probably topologically trivial, this result is interesting against the background of a theoretical prediction from the 1980s about superconductivity induced by doping so-called valence skipping elements: Under certain circumstances (depending on band filling) the presence of such elements bears the potential to further enhance superconductivity due to valence fluctuations (so called "negative-U mechanism"). Here, In is such an element: In SnTe, Sn exhibits a 2+ and Te a 2- state. Hence at first glance In should replace Sn also in a divalent state. However, In^{2+} is energetically unstable, and it is expected to appear as In^{1+}, In^{3+}, or even a mixture of them. According to theory, this could lead to the formation of a charge-density wave at certain doping levels with ordered In-valence states. It is expected that in such a case the superconductivity will be destroyed possibly explaining the two-dome structure in Fig. 1.
In a second step, we also doped Se at the Te site which lead to a further enhancement of T_c to almost 6 K at the In-rich side (not shown in Fig. 1). The latter enhancement is due to doping a lighter element which is expected to rise the underlying phonon frequencies (lattice vibrations) and hence leading to higher superconducting transition temperatures.
This work was published in the Physical Review where it was chosen as an "Editors' Suggestion", see Ref. [3].
In collaboration with theory and scanning-transmission microscopy groups, the complicated low-doped part of the phase diagram, where possibly topological features play a role, was reexamined. According to theoretical calculations, the enhancement of the superconducting T_c at low doping (cf. Fig. 1) can be explained by the strong spin-orbit interaction present in this system. At higher doping towards the suppression of the superconductivity, additional effects such as the mentioned "negative-U mechanism" cannot be ruled out. A publication is currently in preparation.

(2) Discovery of superconductivity in In-doped GeTe

Motivated by the work on In-doped SnTe, In was also doped into isostructural GeTe. The latter is recently discussed to bear potential for topologically nontrivial physics. GeTe exhibits a polar distortion accompanied with a huge Rashba-like spin splitting in the bulk bands up to above room-temperature and exhibits, depending on the dopant, a rich plethora of different interesting physical phenomena. Surprisingly, In doping was not comprehensively examined in the past.
The whole solid solution was successfully prepared, at higher doping levels again by employing a high-pressure synthesis method as in the case of SnTe. Moreover, superconductivity was indeed achieved. However, in spite of the apparent chemical similarities between SnTe and GeTe, the superconducting phase diagram was found to be essentially different, see Fig. 2.
Beside the discovery of superconductivity in this system, we revealed the existence of a multi-critical doping concentration x_c = 0.12 (indicated by the vertical dashed line in Fig. 2), where various properties take either an extremum or change their character: The structure changes from rhombohedral to cubic, the unit-cell volume decreases below and increases above, the resistivity is enhanced by five orders of magnitude, the type of the charge-carriers changes from hole- to electron-like, and the density of states decreases substantially at the dawn of a new superconducting phase which becomes a bulk effect around x = 0.16. Against the background of the valence instability of In, experimental evidence of a change in the In-valence state from In^{3+} to In^{1+} with increasing x was found, suggesting that this system is a new promising playground to probe valence fluctuations and their possible impact on structural, electronic, and thermodynamic properties of their host. Based on our

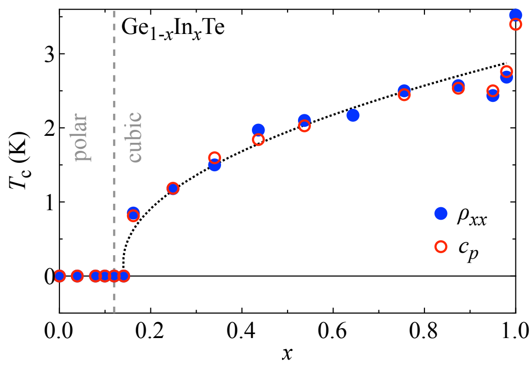

Fig. 2: Superconducting phase diagram of $Ge_{1-x}In_xTe$, see text.

results we were able to propose a model which satisfactorily explains all observed features based on a band picture including the observed crossover in the In valence state. Initially In is doped in its 3+ state in agreement with a shrinking unit-cell volume, the depletion of the initial hole carriers, density of states and an enhanced resistivity. When the doping level crosses the critical concentration x_c = 0.12, In starts to realize its larger 1+ state and hence the unit-cell volume increases again and yields additional density of states giving rise to metallic behaviour and eventually superconductivity. Since this effect stays active over the whole solid solution, this also explains why T_c increases monotonously with x.
This work has been recently submitted to Physical Review Letters.

(3) Dirac semimetal Cd_3As_2

Cd_3As_2 is a well-known long-studied semimetal which got famous for its unusually large mobility in the past. Recently it attracts new interest due to its topological nature: It exhibits a Dirac-like band dispersion as well as a strong and unusual linear magnetoresistive effect.
In collaboration, thin-film samples of Cd_3As_2 were examined in great detail. A new growth method allowed fine-control of the film thickness and crystallinity and the latter turned our to be better than in bulk samples.
Moreover, the theoretically predicted film-thickness dependent phase transitions to a two-dimensional topological insulator and trivial insulator were detected by quantum transport measurements indicating a clear dimensional crossover.
This work was published in Nature Communications and the Physical Review, see Refs. [4] and [5].

(4) Controlling topological Cd_3As_2 by doping

In addition the topological features of Cd_3As_2 were also probed by doping Zn in thin films and in bulk samples. Here the chemical doping in combination with gating the thin films allowed control over the charge carrier concentration and hence a fine-tuning of the Fermi level, i.e., access to the Dirac point of the topological band structure. Doping also drives the system through a phase transition from nontrivial towards the conventional semiconductor Zn_3As_2.
In thin films the two-dimensionality of the Fermi surface was probed and quantum Hall states with different filling factors were successfully observed. Also the suppression of the topological band inversion and the evolution of the negative magnetoresistance in this systems was monitored in detail. The results allow a better understanding of the band structure in this system.
This work was published in Science Advances and the Physical Review, see Refs. [1] and [2].

In bulk samples, a metal-insulator transition was found at intermediate doping levels and the topological phase transition was estimated to happen in the vicinity of $Cd_2Zn_1As_2$. Since it is known that topologically nontrivial systems bear also potential for a good thermoelectrical performance, this solid solution was probed by thermal transport measurements. This work is ongoing but so-far achieved results indicate a promising thermoelectrical performance in this system. A publication is in preparation.

５．主な発表論文等

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〔その他〕
In 2018 I was granted the 9th RIKEN Research Incentive Award and the 5th CEMS Award.

６．研究組織
(1)研究分担者

(2)研究協力者

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