Title	Superconducting Quasicrystals
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Citation	Israel Journal of Chemistry. 2024, 64(10-11), p. e202300124
Version Type	AM
URL	https://hdl.handle.net/11094/93619
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DOI: 10.1002/ijch.200((full DOI will be filled in by the editorial staff))

Superconducting Quasicrystals

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Abstract: Dan Shechtman's discovery of quasicrystals in 1982 introduced the scientific world to aperiodic crystals with unique rotational symmetries, redefining traditional crystallography. Although superconductivity in related periodic approximants has since been observed, true bulk superconductivity in quasicrystals was confirmed only in 2018. This recent discovery opens a new horizon not only for the study of correlated quasicrystals but more generally for the study of superconductivity with nontrivial spatial order. The theoretical understanding of superconducting quasicrystals poses challenges due to their lack of periodicity. Notably, they exhibit non-BCS type superconductivity and distinct electromagnetic responses, reminiscent of the so-called FFLO state. In this review, we provide an overview of superconducting quasicrystals, along with some "behind-the-scenes" information.

Keywords: quasicrystals • superconductivity • electron correlation effect• physical property

1. Introduction

In 1982, Dan Shechtman made a groundbreaking discovery when he observed 5-fold rotational symmetry in a Bragg reflection image of a quenched Al-Mn alloy [1]. This diffraction pattern differed significantly from that of an amorphous solid, exhibiting Bragg peaks thus indicating the presence of long-range order, although it was inconsistent with periodicity owing to its 5-fold rotational symmetry. Subsequent experiments, employing high-resolution electron microscopy, confirmed the existence of crystals without periodicity but possessing sharp Bragg peaks in the diffraction images. These newly discovered solid-state structures, with quasiperiodic rather than periodic long-range order, were named "quasicrystals" for short by Levine and Steinhardt [4].

The recognition of quasicrystals as ordered structures faced some initial skepticism. However, in 1992, the International Union of Crystallography revised the definition of a crystal to "any solid having an essentially discrete diffraction diagram." [5] thereby accepting quasicrystals as a legitimate form of crystal. Shechtman's pioneering work earned him the Nobel Prize in Chemistry in 2011 for this significant discovery.

The lack of periodicity enables quasicrystals to exhibit high rotational symmetries [6-8], such as 8-fold and 10-fold. These property gives rise to nontrivial metallic behavior, exemplified by unusually high electrical resistivities [9] and thermal resistivities [10]. Those atypical features make quasicrystals a fascinating and important subject of research in the field of condensed matter physics.

In 2011, a so-called Tsai-type quasicrystal $Au_{51}Al_{34}Yb_{15}$, containing the f-electron element Yb, was successfully synthesized [11]. This quasicrystal proved to be the first one to exhibit strongly correlated electron phenomena. Studies indicated that the ytterbium ions in this material have an intermediate valence, ranging from Yb^{2+} to Yb^{3+}, suggesting that Yb atoms contribute both localized and itinerant electrons [12].

Further investigations revealed intriguing low-temperature properties of the quasicrystal $Au_{51}Al_{34}Yb_{15}$ [13]. Its magnetic susceptibility χ exhibited non-trivial power-law behavior, following $\chi \propto T^{-0.5}$, and the specific heat coefficient γ showed a logarithmic divergence, with $\gamma \propto -\ln T$, at low temperatures. These findings pointed towards quantum critical behavior within the quasicrystal. Notably, this quantum criticality persisted even under applied hydrostatic pressure, setting it apart from conventional behavior.

In contrast, the approximant $Au_{51}Al_{35}Yb_{14}$, which has a composition similar to the quasicrystal but is a periodic crystal, displayed conventional heavy fermion behavior. It exhibited a specific heat coefficient hundreds of times larger than that of a free electron and showed quantum criticality only at a pressure of 1.96 [GPa] [14].

These pioneering experiments paved the way for interdisciplinary research exploring correlated electrons in quasicrystals. Among the various topics, superconductivity in quasicrystals emerged as one of the most intriguing and captivating areas of study. This review aims to provide a

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comprehensive overview of the current knowledge and progress surrounding superconducting quasicrystals.

Nayuta Takemori began her academic journey at the Tokyo Institute of Technology, where she specialized in studying correlated electron states peculiar to quasiperiodic systems. After completing her doctoral studies in 2015, she held various research positions, including a role as a Special Postdoctoral Researcher at RIKEN from 2016 to 2017. Subsequently, she served as a Specially Appointed Assistant Professor at Okayama University from 2017 to 2021. In 2021, she joined Osaka University as a Specially Appointed Associate Professor and was later promoted to the position of Associate Professor in 2023.

2. Experimental observation of superconductivity in quasicrystals and some behind-the-scenes

Initially, after the discovery of quantum criticality in $Au_{51}Al_{34}Yb_{15}$, several superconducting approximants of Tsai-type materials such as Au-Ge-Yb approximants, which contains non-magnetic/magnetic ions at the very center of the cluster were identified [15]. The critical temperature is 0.68K in $Au_{64.0}Ge_{22.0}Yb_{14.0}$ with non-magnetic cluster center and 0.36K for $Au_{63.5}Ge_{20.5}Yb_{16.0}$ with magnetic cluster center. Also, superconductivity in some periodic approximant were discovered in subsequent studies such as Y-Au-Si approximant [16]. However, the observation of bulk superconductivity in quasicrystals did not occur until 2018. As a behind-the-scenes, some publications already reported the discovery of superconducting quasicrystals, but they lacked sufficient evidence to support bulk superconductivity in *true* quasicrystals. One example of this is a report published only few years later the discovery of quasicrystals [17], which was later confirmed by subsequent experiments to be an approximant [18].

In 2018, a significant breakthrough was made again with the discovery of bulk superconductivity in a so-called Bergmann-type Al-Mg-Zn quasicrystalline alloy [19]. The properties measured in this alloy exhibited characteristics consistent with a weak-coupling superconductor. The evidence supporting bulk superconductivity in quasicrystals included a diffraction pattern displaying five-fold rotational symmetry, zero resistivity, and the Meissner effect, which are direct evidence of superconductivity. Furthermore, the specific heat measurements provided further evidence of bulk superconductivity.

The important point is that they concluded that the superconductivity in this quasicrystal was of the weak-coupled type, as it closely aligned with the specific heat predictions from the BCS theory, except for a slight deviation with a 23% smaller specific heat jump. This work provided the necessary evidence to confirm the existence of bulk superconductivity in quasicrystals and shed light on their intriguing superconducting properties.

3. Theoretical investigation on superconducting quasicrystals

In the pursuit of unraveling the fascinating world of superconductivity in quasicrystals, theoretical investigations have also played a crucial role in deepening our understanding. Even before the experimental discovery of bulk superconductivity in quasicrystals, there is a pioneering work by assuming an direct electron-electron interactions, leading to the emergence of exotic superconductivity [20]. This laid the foundation for exploring the theoretical framework of correlation effects in quasicrystals, as well as diverse aspects of s-wave superconductivity and the intriguing phenomena associated with it.

3.1. Theoretical framework for correlation effects in quasicrystals

The theoretical investigation of quasicrystals poses greater challenges compared to periodic crystals due to the inapplicability of the Bloch theorem. There are two primary theoretical approaches: one involves studying periodic approximants through first-principles calculations [21,22], with a focus on the role of local structure rather than quasiperiodicity. However, this approach struggles to account for strong electronic correlations. The other approach explores toy models, such as the tight-binding model [23-26], the Heisenberg model [27-29], and the Hubbard model [20, 30-32], on quasiperiodic tiling. In the former case, conventional k-momentum based methods can be directly applied to the system, but the handling of real-space systems becomes necessary. In such cases, the real-space extension of the dynamical mean-field theory (RDMFT) [20, 30, 33] or the Bogoliubov de Gennes (BdG) equation [34,35] can be employed.

Furthermore, to comprehensively investigate the behavior of quasicrystals, particularly at very low temperatures, one can make use of real-space dual fermion approach [36], which enables us to study intersite electron correlation effects in various other inhomogeneous systems such as cold atoms in a trapping potential, nanosystems, topological insulators and quasiperiodic tiling.

3.2. Theoretical investigation on s-wave superconductivity

The extensive theoretical analyses of attractive Hubbard model, where the key parameters are the on-site Coulomb attractive interaction U, the hopping parameter $\boldsymbol{t} = \mathbf{1}$ and n is the averaged electron density, conducted on Penrose tiling have revealed the properties of Cooper pairs in quasicrystals. This leads to the real-space distributions of the site-dependent local electron density and superconducting order parameter [20, 34, 36-45]. More interestingly, it has been pointed out that non-BCS type superconductivity, comprised of Cooper pairs with finite center-of-mass momentum (Fig. 1), exists in the weak-coupling region [20].

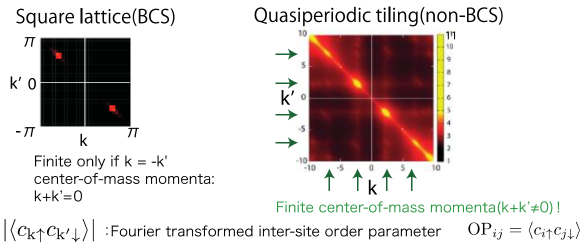

Figure 1. Cooper pairs of finite center-of-mass momentum in quasicrystals in comparison with BCS superconductivity.

Considering these findings, the question arises as to whether this quasiperiodic superconductor exhibits any distinct properties, particularly those that can be experimentally observed and differ from the behaviors observed in BCS superconductors. To address this question comprehensively, the study proceeds to calculate experimentally observable quantities, such as the specific heat and current-voltage characteristics, as well as several fundamental quantities characterizing the superconductors [35]. The investigation reveals intriguing results: the specific heat jump is found to be approximately 10%-20% smaller compared to that obtained with the BCS theory due to the lack of periodicity (Fig. 2). Additionally, the current-voltage (I-V) curve exhibits a gradual increase in the case of Penrose tiling, which significantly differs from the rapid increase given by the BCS theory. These observations prompt further experimental investigations into these quantities in quasicrystalline superconductors, providing valuable insights into the unique behaviors and properties of these fascinating materials.

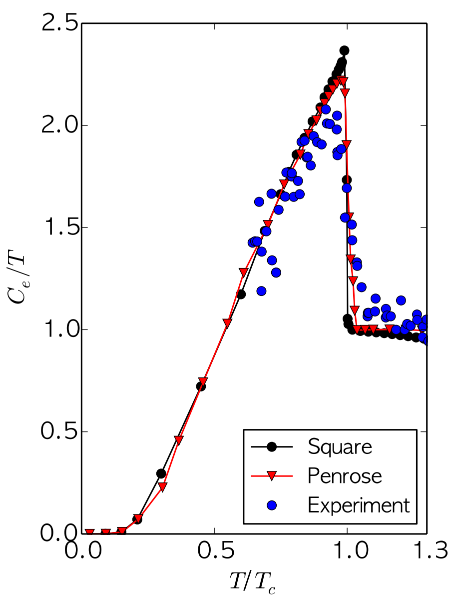

Figure 2. Comparison of the temperature dependence of the specific heat C_e/T obtained from square lattice and Penrose tiling ($U = -3$,1/4 filings) with experimental results. Note that the specific heat is given in units of C_{en}/T_c, where C_{en} is the specific heat of the normal state at T_c.

In related studies, *ab initio* calculations have provided valuable insights into the electronic structure of the periodic approximants of the Al-Zn-Mg superconductor [22]. These calculations have also contributed to understanding the origin of the small specific heat in Al-Mn-Zn quasicrystal, which is associated with the pseudo-gap phenomenon. To clarify the origin of the small specific heat, further comparisons of specific heat in various approximants and quasicrystals are necessary.

Other recent theoretical studies have proposed possible exotic superconductivities, like the sign-alternating pairing under the magnetic field [42] and topological superconductivity in quasicrystal [40,44].

3.3. Supercurrents in s-wave superconducting quasicrystals

It is quite interesting to consider the effect of electromagnetic response in quasiperiodic superconductors. Since the Cooper pair holds finite center-of-mass momentum, the supercurrent is expected to show a finite contribution from the paramagnetic current even at zero temperature. This can be naturally understood by considering the expectation value of the Cooper pair velocity $\boldsymbol{v}$ in terms of finite canonical momentum $\boldsymbol{p} = \boldsymbol{m}^*\boldsymbol{v} + \boldsymbol{e}^*\boldsymbol{A}/\boldsymbol{c}$ under the uniform vector potential, which is consisted of additional term other than the diamagnetic current as a response term proportional to the vector potential. Here, $\boldsymbol{m}^*$ and $\boldsymbol{e}^*$ denote the mass and the electric charge of the Cooper pair, and $\boldsymbol{A}$ denotes vector potential and $\boldsymbol{c}$ denotes light velocity. An example of such behavior has been clarified in the site-averaged paramagnetic current on Penrose tiling by Liu *et al.*, [45] independent of the above considerations.

Indeed, recent work [46,47] reveals on Ammann-Beenker tiling an intriguing characteristic of the diamagnetic current in quasicrystalline superconductors: it locally violates the current conservation law. To compensate for this violation, the paramagnetic current also comes into play, even at absolute zero temperature. As a result, the paramagnetic component displays several notable anomalies, differentiating it from conventional periodic superconductors.

One significant finding is the anomalous flow of the paramagnetic current perpendicular to the applied vector potential (Fig. 3). This behavior deviates from what is typically observed in periodic superconductors, highlighting the distinct response of quasicrystalline superconductors to electromagnetic perturbations.

Another remarkable feature is the persistence of the paramagnetic current at zero temperature, regardless of the flow direction [47]. Unlike in periodic superconductors, where the paramagnetic current vanishes at absolute zero temperature, quasicrystals exhibit this finite paramagnetic current behavior due to the involvement of Cooper pairs with finite center-of-mass momentum. This characteristic is reminiscent of the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state [48,49], known for its formation of superconducting states with non-zero center-of-mass momentum.

Overall, these findings shed light on the intriguing electromagnetic response of quasicrystalline superconductors, unveiling the unique interplay between diamagnetic and paramagnetic currents. The presence of paramagnetic currents flowing perpendicular to the applied vector potential and their finite existence at absolute zero temperature in quasicrystals contribute to the diverse landscape of superconducting behaviors in these captivating materials. The understanding and manipulation of these unconventional supercurrent properties offer exciting opportunities for further exploration of the underlying physics of quasicrystalline superconductors.

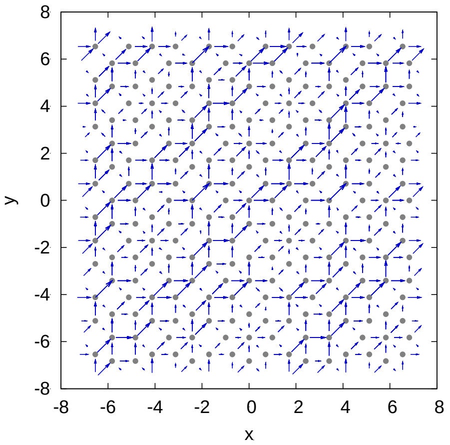

Figure 3. Real-space distribution of the local supercurrent on Ammann-Beenker structure for $n = 0.3$ and $U = -3$. The direction of applied phase modulation is $\theta = \frac{\pi}{8}$.

4. Outlook

In this review, we summarize the recent research on superconducting quasicrystals. It is already quite astonishing that the existence of the superconductivity in quasicrystals have been confirmed, however, further investigation such as specific heat measurement, transport property measurements and tunneling spectroscopy, is necessary to confirm the non-BCS type superconductivity predicted theoretically.

Additionally, there are several papers [43, 50] focusing on the anisotropic superconductivity, which will undoubtedly be a trend in quasicrystalline superconductivity in the future. Beyond quasicrystals, recent studies have begun exploring superconductivity in systems with quasiperiodic structures, such as twisted layers of graphene [51]. Such explorations are vital in understanding the broader implications of quasiperiodicity in superconducting materials and may pave the way for novel superconducting phenomena.

Acknowledgements

N. T. is supported by JSPS KAKENHI Grant No. JP19H05817, JP19H05820, JST PRESTO No. JPMJPR23F6, and JST (COI-NEXT) Grant No. JPMJPF2014.

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Received: ((will be filled in by the editorial staff))
Accepted: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))