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Editorial

Superconducting materials classes: Introduction and overview

ABSTRACT

An introduction to and overview of the contents of this Special Issue are given. 32 classes of superconducting materials are discussed, grouped under the three categories “conventional”, “possibly unconventional” and “unconventional” according to the mechanism believed to give rise to superconductivity.

1. Introduction

In this Special Issue we aim to give a comprehensive overview of the superconducting materials known to date. Superconducting materials were grouped into 32 different classes, and we invited recognized experimental leaders in each class, including in many cases individuals who discovered a new class of superconductors, to contribute an article giving an overview of the properties of that class. We were fortunate to get an excellent response.

By a “class” we mean a set of materials with common or closely related crystal structure, composition and physical properties, and hence presumably the members of a class exhibit superconductivity driven by the same physical mechanism. There is at present no general understanding of the mechanism(s) giving rise to superconductivity in many of these classes. The purpose of this Special Issue is to put together in one place essential information on the multiple different classes of superconductors, to facilitate comparison of the commonalities and differences in the physical properties of the different classes that may be playing a role in the superconductivity.

It is not uncommon that superconductivity researchers concentrate their efforts on one or at most a small number of classes of superconductors, and are unaware of relationships that may exist with other classes. We hope that this compendium will facilitate making connections between the different classes of superconductors, thus helping researchers identify which properties are linked to superconductivity of a given class and which are not. We hope that this will contribute to the ultimate goal of understanding what are the mechanisms of superconductivity that explain all the types of superconductors found in nature, and as a consequence aid in the search for new superconducting materials with desirable properties, particularly higher T_c’s.

The classes have been grouped into three categories: “conventional superconductors”, “possibly unconventional superconductors” and “unconventional superconductors”. For materials in the first category, there is broad consensus that they are described by conventional BCS-Eliashberg-Migdal theory of superconductivity, driven by the electron–phonon interaction. For materials in the third category, there is broad consensus that they are not described by the conventional theory, either because T_c is too high or because some physical properties point to a different mechanism. However, there is no consensus on which new mechanism(s) explain the various different classes of unconventional superconductors. For materials in the second category, the evidence in favor of the conventional mechanism is mixed. We asked the authors themselves to tell us in which of these three categories they felt that their paper should be included and in most cases followed their recommendation. In cases where we did not receive input from the authors on this question we followed our best judgement.

We asked the authors to address for their class various normal and superconducting state properties, and in particular signatures of conventional or unconventional superconductivity. The emphasis was to be on experimentally known properties, but since many of these measurements are motivated by an underlying theoretical framework, authors were also asked to summarize theoretical ideas, such as band structure calculations, and proposed or currently accepted theoretical explanations. We also asked the authors to address commonalities and differences of their class with other classes that they felt may be related. Finally, we asked authors to provide key references for each class including earlier reviews as sources of additional information for the reader.

From the time superconductivity was discovered in 1911 until BCS theory was developed in 1957, many attempts at theories of superconductivity were made [1]. The search during that period was for “the” theory of superconductivity, since it was believed that a single theory would explain all the many superconducting elements and compounds already known at that time. After BCS theory was proposed, there were initially some suggestions that the BCS electron–phonon induced pairing mechanism may apply to most but not all superconductors [2,3], as reviewed in the contribution by Geballe et al. [4] in this volume. However, theoretical explanations within BCS theory were found for the anomalies that prompted these suggestions, and by the time Parks’ [5] influential treatise on superconductivity was published in 1969 and for about 10 years thereafter, it was generally believed that BCS-Eliashberg-electron–phonon theory described all superconducting materials.

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Nonetheless, some theoretical suggestions were made during the 1960s and early 1970s [6,8,7] that in some specially designed materials non-electron–phonon pairing mechanisms (“excitonic”) could give rise to superconductivity, potentially at higher temperatures, but no clear experimental evidence for such materials was found.

The situation began to change in the mid-1970s. The first material with a strong claim to be an “unconventional superconductor” was discovered by Sleight and coworkers in 1975 [9], $BaPb_{1-x}Bi_xO_3$, with a surprisingly high T_c (13 K) given its low density of states. A few years later, “heavy fermion” superconductors were discovered in 1979 and organic charge transfer salts in 1980, both showing strong evidence for a non-s-wave order parameter. These were followed by the high T_c cuprates in 1986, and many other classes of unconventional or possibly unconventional superconductors in the ensuing years. There is at this time no doubt in anybody’s mind that the conventional BCS-Eliashberg-electron–phonon theory of superconductivity is *not* applicable to all superconductors.

It should not go without mention that Bernd Matthias, a prodigious researcher who discovered many new superconducting materials in the period 1950–1980 guided by empirical rules that he devised, had been vehemently advocating the possibility of mechanisms other that the electron–phonon interaction to explain the superconductivity of various materials during the 1960s and 1970s [10,11]. He passed away in 1980, right before the field of unconventional superconductivity would take off, but his legacy lives on as the reader will see in many articles in this Special Issue.

One of Matthias’ closest collaborators during that early period was Ted Geballe, one of the authors of this Special Issue. Ted has contributed longer than anybody else to the knowledge in this field over a distinguished 65 year scientific career, making numerous seminal contributions to the discovery and understanding of many superconducting materials covered in this volume. The editors would like to dedicate this Special Issue to Ted on the year of his 95th birthday.

In the remaining part of this introductory article we provide a brief overview of the contents of this Special Issue. In Table 1, we list the classes of materials, the year of discovery, the highest T_c in the class, some physical properties, and whether it is believed to be conventional, possibly unconventional, or unconventional. A timeline Fig. 1 summarizes progress to date.

2. Overview

The article following this Introduction, “What T_c tells” [4], by Geballe, Hammond and Wu, proposes that the value of T_c itself as well as the response of T_c to various parameter changes such as ionic mass, composition, pressure or structure can give valuable clues on the superconductivity mechanism. It discusses selected examples of this idea for both conventional and unconventional materials and in so doing gives a nice overview of the historical development of the field of superconducting materials. The authors also discuss negative U centers as a possible non-conventional pairing mechanism relevant to superconductivity of certain materials.

The ensuing 32 articles cover each a different materials class, written by distinguished experimentalists in each class. In the following we briefly discuss the 32 classes of materials with 12, 9 and 11 classes in the C (conventional), P (possibly unconventional) and U (unconventional) categories, respectively. By clicking on the class number (e.g. C1) the reader will be directed to the paper discussing that class.

In the closing section of this Special Issue, Greg Stewart[12], a former Ph.D. student of Ted Geballe, provides us with some highlights of Ted’s illustrious career. Finally, we have included an Epilogue[13], where several major experimental contributors to the field of superconducting materials have shared their views on past accomplishments and future hopes in this field.

2.1. Conventional superconductors

C1: The first article in this category, “Superconductivity in the elements, alloys and simple compounds” by Webb et al. [14], gives a review of the earliest superconducting materials discovered, that were known when BCS theory was proposed, and describes the extensions of BCS theory to include the retarded nature of the phonon-induced effective electron–electron interaction, necessary for the understanding of deviations of the properties of these materials from the predictions of simple BCS theory. It also recounts the successes and failures of theoretical efforts to explain the observed T_c’s of elements and simple compounds using this theoretical framework.

C2: The second article by Stewart [15] reviews the A15 compounds, discovered in 1954. The A15’s are distinguished by the fact that for over 30 years they were the highest T_c materials known, and they were and are today the superconductors that are used in many high magnetic field applications. They are believed to be almost prototypical Eliashberg electron–phonon driven superconductors, except that phonon anomalies seem to add some interesting wrinkles, and peaks in the electronic density of states at the Fermi level play an important role in the quantitative understanding of their properties. Stewart makes a number of interesting comparisons with other superconducting families, not the least of which is that Cs_3C_{60}, a doped fullerene that becomes superconducting at 38 K only under pressure, actually adopts an A15 lattice structure. This also makes it a member of the growing family of materials that are insulating at ambient pressure but superconducting under pressure.

C3: The third article by Bustarrett [16] reviews doped semiconductors, a class discovered in the 1960s that underwent a revival of interest starting in the mid-1990s when higher T_c materials were found. The carrier concentration in these materials is very low; for the most part, they are understood within the conventional framework (hence we included them in the first category), but the author notes that there are some puzzles such as Tl-doped PbTe that may require a different mechanism, as also discussed by Geballe et al. in their article.

C4: The 31 known superconducting elements at ambient pressure are metals. In 1964 the first non-superconducting element to become superconducting under pressure was discovered, Te, a semiconductor at ambient pressure. Since then, many other semiconducting and insulating elements have been found to become metallic and superconducting at high pressures, as reviewed by Shimizu [17] in the fourth article. The highest T_c among insulating elements under pressure is sulfur with $T_c = 17$ K. The superconductivity in this class is understood to arise from the conventional electron–phonon mechanism.

C5: Superconductivity in graphite intercalation compounds is reviewed in the fifth article, by Smith et al. [18]. The first material in this class was discovered in 1965. The authors review the early history of these materials, which have T_c’s of a few K, and the recent revival of interest with the discovery of superconductivity in C_6Ca and C_6Yb, with T_c’s up to 12 K. They discuss the important role of dimensionality and charge transfer, the difficulties in understanding the different role for the superconductivity of the intercalant metal band versus the graphite π and π^* bands arising from C p_z orbitals, and the conflicting information from the large Ca isotope shift observed in C_6Ca. The authors state that the pairing mechanism has always been an open question. Nevertheless, we included this class in the first category because theoretical work on these materials has focused on the conventional mechanism.