Physica C 514 (2015) 17–27

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Superconductivity in the elements, alloys and simple compounds

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ARTICLE INFO

Article history:
Received 3 February 2015
Received in revised form 10 February 2015
Accepted 12 February 2015
Available online 27 February 2015

Keywords:
Conventional superconductors
Elements
Alloys
Simple compounds
BCS–Eliashberg
Electron–phonon

ABSTRACT

We give a brief review of superconductivity at ambient pressure in elements, alloys, and simple three-dimensional compounds. Historically these were the first superconducting materials studied, and based on the experimental knowledge gained from them the BCS theory of superconductivity was developed in 1957. Extended to include the effect of phonon retardation, the theory is believed to describe the subset of superconducting materials known as 'conventional superconductors', where superconductivity is caused by the electron–phonon interaction. These include the elements, alloys and simple compounds discussed in this article and several other classes of materials discussed in other articles in this Special Issue.

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1. Introduction

Superconductivity was discovered by Kamerlingh Onnes in 1911 in Hg [1], and in Pb and Sn within the next two years [2]. By 1932, Tl, In, Ga, Ta, Ti, Th and Nb had also been found to be superconductors [3]. By 1935, 15 superconducting elements were known [4], 19 by 1946 [5], 22 by 1954 [6]. Today, 31 elements are known to be superconducting at ambient pressure [7,8], many more at high pressures [9]. Critical temperatures of the elements at ambient pressure range from 0.0003 K for Rh to 9.25 K for Nb.

Shortly after superconductivity in Hg was discovered in 1911, alloys of HgAu, HgCd HgSn and PbSn were also measured and found to be superconducting [2]. By 1932 [3], a large number of binary alloys and compounds had been found to be superconducting including Au_2Bi, with both elements non-superconducting [10]. It was also found that when alloying a non-superconducting metal with a superconducting one T_c may be increased. Superconducting binary compounds with one of the elements nonmetallic were found [3], e.g. NbC, with $T_c = 10.1$ K, a non-superconducting metal with an insulator, CuS, $T_c = 1.6$ K [11] and many other binary

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http://dx.doi.org/10.1016/j.physc.2015.02.037
0921-4534/

Table 1
Some superconducting alloys and compounds known in 1935 [4].

Material	T_c	Material	T_c
Bi_6Tl_3	6.5 K	TiN	1.4 K
Sb_2Tl_7	5.5	TiC	1.1
Na_2Pb_5	7.2	TaC	9.2
Hg_5Tl_7	3.8	NbC	10.1
Au_2Bi	1.84	ZrB	2.82
CuS	1.6	TaSi	4.2
VN	1.3	PbS	4.1
WC	2.8	Pb–As alloy	8.4
W_2C	2.05	Pb–Sn–Bi	8.5
MoC	7.7	Pb–As–Bi	9.0
Mo_2C	2.4	Pb–Bi–Sb	8.9

compounds, particularly sulfides, nitrides and carbides [3]. These early findings demonstrated that superconductivity is a property of the solid, not of the elements forming the solid. Table 1 gives examples of superconducting compounds discussed in a 1935 review [4].

These experimental results indicated that the energy scale associated with superconductivity was of order $k_BT_c \sim 10^{-4}$ eV. On the other hand, it was generally believed at the time that superconductivity originated from the electron–electron interaction neglected in Bloch's theory of electrons in single-particle energy bands. Thus a major puzzle was to understand how an interaction many orders of magnitude larger could give rise to the low T_c's measured experimentally.

In Table 2 we list the 19 superconducting elements known by the year 1946, from a paper by Justi [5]. The table also gives the Debye temperatures as given in that paper. It is interesting that Justi discusses in this paper the possible effect of the ionic mass and Debye temperature on the critical temperature. He reasoned that because lattice vibrations give rise to Ohmic resistance, one might expect a connection between Debye temperature and superconducting T_c. However, from the data in Table 2 he concluded that there is no relation between θ_D and T_c [5]. In addition he discussed an experiment performed in 1941 [12] attempting to detect any difference in the critical temperature of the two Pb isotopes ^{206}Pb and ^{208}Pb and finding identical results to an accuracy 1/1000. From these observations he concluded in 1946 that the ionic mass has no influence on superconductivity.

The possible relation between Debye temperature and superconducting critical temperature was also examined by de Launay

Table 2
Critical temperature and Debye temperature of superconducting elements known in 1946 [5].

Metal	T_c	θ_D
Nb	9.22	184
Pb	7.26	86
La	4.71	?
Ta	4.38	246
V	4.3	69
Hg	4.12	69
Sn	3.69	180
In	3.37	150
Tl	2.38	100
Ti	1.81	400
Th	1.32	200
U	1.25	141
Al	1.14	305
Ga	1.07	125
Re	0.95	283
Zn	0.79	230
Zr	0.70	288
Cd	0.54	158
Hf	0.35	?

Table 3
Critical temperature, Debye temperature, atomic mass, measured and calculated isotope exponents of superconducting elements. Measured values are taken from a table in Ref. [22] and theoretical values are taken from a table in Ref. [23].

Metal	T_c	θ_D	M	α	α_{theory}
Nb	9.25	275	93		
Tc	8.2	450	99		
Pb	7.2	105	207	0.48	0.47
La	6	142	139		
V	5.4	380	51		0.15
Ta	4.4	240	181		0.35
Hg	4.15	72	201	0.5	0.465
Sn	3.7	200	119	0.46	0.44
In	3.4	108	115		
Tl	2.4	78.5	204	0.5	0.445
Re	1.7	430	186	0.38	0.3
Th	1.4	163	232		
Pa	1.4	185	231		
U	1.3	207	238	−2	
Al	1.18	428	27		0.345
Ga	1.08	320	70		
Am	1	154	243		
Mo	0.92	450	96	0.37	0.35
Zn	0.85	327	65	0.3	
Os	0.7	500	190	0.21	0.1
Zr	0.6	291	91	0	0.35
Cd	0.52	209	112	0.5	0.365
Ru	0.5	600	101	0	0.0
Ti	0.5	420	48		0.2
Hf	0.38	252	176		0.3
Ir	0.1	420	192		−0.2
Lu	0.1	210	139		
Be	1440	1440	9		
W	0.01	400	184		
Li	0.0004	344	7		
Rh	0.0003	480	103		

and Dolecek in 1947 [13]. In their paper "Superconductivity and the Debye characteristic temperature" they plotted the critical temperature versus Debye temperature. From this they concluded that electronegative elements have T_c's well above the T_c's of electropositive elements of comparable Debye temperatures, except in the range of lowest Debye temperatures where they converge. Combining these data with the atomic volumes they predicted that, at atmospheric pressure, scandium and yttrium should not be superconducting (correct) and that Ce, Pr and Nd should be superconducting (incorrect).

In view of these investigations it is remarkable that just three years later in 1950 Herbert Fröhlich proposed [14] that superconducting critical temperatures should be proportional to $M^{-\alpha}$, with M the ionic mass and $\alpha = 0.5$ the isotope exponent. This was done without knowledge [15–17] of the isotope effect experiments [18,19] being conducted at the same time that measured an isotope exponent $\alpha \sim 0.5$ in Hg and shortly thereafter in Pb [20], Sn and Tl [21]. Table 3 lists the isotope exponents of these and several other elements measured since then [22,23].

After the experimental findings of an isotope effect, the focus of theoretical efforts to understand the origin of the interaction leading to superconductivity shifted from the electron–electron interaction to the electron–phonon interaction. In 1957 BCS developed their theory based on an effective instantaneous attractive interaction between electrons mediated by phonons [24], that also predicts $\alpha = 0.5$. BCS theory, extended to take into account the fact that the effective interaction between electrons mediated by phonons is not instantaneous but retarded, is believed to describe the superconductivity of all elements at ambient pressure, and of thousands of superconducting compounds. The tabulation by Roberts (1976) [25] lists several tens of thousands of superconducting alloys and compounds, almost all with critical temperatures below 20 K, believed to be described by BCS theory.