Physica C 514 (2015) 28–35

Contents lists available at ScienceDirect

Physica C

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

Superconductivity in the A15 structure

G.R. Stewart

Department of Physics, University of Florida, Gainesville, FL 32611, United States

ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form 3 January 2015
Accepted 15 February 2015
Available online 24 February 2015

Keywords:
A15 structure
Superconductivity
High T_c superconductivity

ABSTRACT

The cubic A15 structure metals, with over 60 distinct member compounds, held the crown of highest T_c superconductor starting in 1954 with the discovery of $T_c = 18$ K in Nb_3Sn. T_c increased over the next 20 years until the discovery in 1973 of $T_c = 22.3$ K (optimized to ≈23 K a year later) in sputtered films of Nb_3Ge. Attempts were made to produce – via explosive compression – higher (theorized to be 31–35 K) transition temperatures in not-stable-at-ambient-conditions A15 Nb_3Si. However, the effort to continue the march to higher T_c's in A15 Nb_3Si only resulted in a defect-suppressed T_c of 19 K by 1981. Focus in superconductivity research partially shifted with the advent of heavy Fermion superconductors ($CeCu_2Si_2$, UBe_{13}, and UPt_3 discovered in 1979, 1983 and 1984 respectively) and further shifted away from A15's with the discovery of the perovskite structure cuprate superconductors in 1986 with $T_c = 35$ K. However, the A15 superconductors – and specifically doped Nb_3Sn – are still the material of choice today for most applications where high critical currents (e.g. magnets with dc persistent fields up to 21 T) are required. Thus, this article discusses superconductivity, and the important physical properties and theories for the understanding thereof, in the A15's which held the record T_c for the longest time (32 years) of any known class of superconductor since the discovery of $T_c = 4.2$ K in Hg in 1911. The discovery in 2008 of $T_c = 38$ K at 7 kbar in A15 Cs_3C_{60} (properly a member of the fullerene superconductor class), which is an insulator at 1 atm pressure and otherwise also atypical of the A15 class of superconductors, will be briefly discussed.

Contents

1. Introduction 28
2. Discussion of A15's as a class of superconductor 29
   2.1. A15's from a materials perspective 29
   2.2. Theoretical understanding of superconductivity in the A15's 30
   2.3. Important physical properties 32
   2.4. Attempts to exceed $T_c = 23$ K in Nb_3Ge: A15 Nb_3Si 34
   2.5. Comparison of A15's with other superconductor classes; summary 34
   Acknowledgements 34
   References 35

1. Introduction

Until the discovery [1] by Hardy and Hulm of 17.1 K superconductivity in cubic A15 structure V_3Si in March 1954, the cubic NaCl structure class of materials had had no competition for the record highest T_c. The upwards climb of T_c in the NaCl structure materials began with $T_c = 10.3$ K in [2] 1933 for NbC, followed by 15.25 K in [3] NbN in 1942 [4] (15.98 K in 1952 [5]). Matthias reported [6] (essentially at the same time as the discovery of superconductivity in V_3Si) $T_c = 17.8$ K in November 1953 for $NbC_{0.3}N_{0.7}$, but the record T_c passed to the A15's in September 1954 (for [7] Nb_3Sn, $T_c = 18.05 \pm 0.1$ K) and stayed with the A15's until 1986. There were other 'high' T_c materials discovered during this period (e.g. bcc Pu_2C_3 structure $Y_{0.7}Th_{0.3}C_{1.5}$, $T_c = 17$ K in [8] 1969), but A15's were

http://dx.doi.org/10.1016/j.physc.2015.02.013
0921-4534/

by far the much larger class and the main focus in the search for higher T_c during this period. After the discovery of what was at the time 'high temperature' superconductivity in V_3Si and Nb_3Sn only six months apart, the search for other examples in the A15's with higher T_c did not progress for more than a decade. Then, T_c was found to be 20.0 K in $Nb_3Al_{0.8}Ge_{0.2}$ in [9] 1967, 18.8 K in Nb_3Al in [10] 1969 (previously 18 K [11] 1959), 20.3 K in Nb_3Ga in [12] 1971 and finally 22.3 K in Nb_3Ge in [13] 1973, optimized to 22.9 K in [14] 1974 (23.2 K in Ref. [15]).

This article is intended to give an overview of the A15 class of superconductors, which (despite being bypassed in the quest for higher T_c by the cuprates in 1986, by MgB_2 in 2001, and by the iron based superconductors in 2008) remain the leader in applications (e.g. medical imaging) requiring magnets with fields larger than 10 T. Considered to be conventional, BCS superconductors, the study of the A15's led to important insights as to the causes of electron–phonon mediated superconductivity and also progress in materials preparation and characterization which has been useful in studying and applying the succeeding classes of superconductors.

For ease of navigation for the reader, the discussion on A15's in Section 2 below is divided into five sections: 1. materials preparation and properties/structure/applications; 2. theoretical understanding of why T_c is so high; 3. important properties: resistivity, susceptibility, specific heat, upper critical field, other; 4. attempts to go past T_c = 23 K in Nb_3Ge: A15 Nb_3Si; 5. comparison of the conventional A15 superconductors with other classes of superconductors and summary.

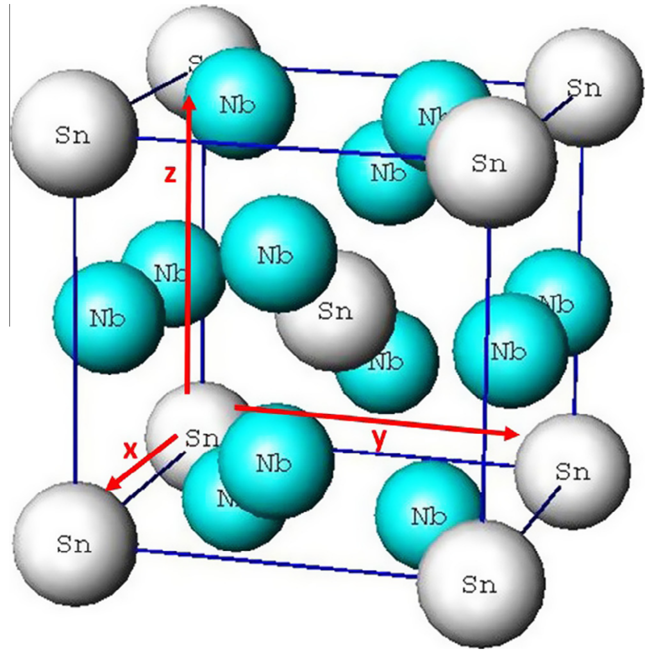

Fig. 1. Diagram [16] of A15 Nb_3Sn, which has a cube edge (lattice parameter 'a_0') of length 5.29 Å. The B atoms form a body centered cube, and the A atoms form one dimensional chains in the three orthogonal directions, with an interatomic spacing along the chains of 1/2 of the lattice parameter. For A15 Nb_3Sn, this gives a Nb–Nb spacing much closer (7.5%) than in, e.g., pure Nb which has the highest elemental T_c at 9.2 K. This rather unique structure has an important influence on the physical properties (including electronic density of states at the Fermi energy, N(0), and the phonon spectrum), as will be discussed in the theoretical understanding section. Some samples of Nb_3Sn and V_3Si exhibit [17] a martensitic phase transformation from cubic → tetragonal upon cooling, discussed below in Section 2.2.

2. Discussion of A15's as a class of superconductor

2.1. A15's from a materials perspective

The cubic A15 structure, pictured in Fig. 1, is also called β-W since the first observation of the structure in 1931 was in an allotrope of tungsten. The prototypical A15 compound is the non-superconducting Cr_3Si. Although there are often variations of stoichiometry, the ideal formula unit is A_3B, where A is a transition metal like V, Nb, or Mo and B is from the right side of the periodic table, including elements like Al, Si, Ge and Sn. Some examples of A15's have stoichiometries far from the canonical A_3B, e.g. $Mo_{0.4}Tc_{0.6}$ (T_c = 13.4 K [18]) and $V_{0.29}Re_{0.71}$ (T_c = 8.4 K [19]) with B atoms on the A-sites, and $Nb_3(Nb_{0.92}Ge_{0.08})$ or 'Nb_3Nb' stabilized in the A15 structure by a few percent Ge, T_c = 5.2 K [20], with A atoms on the B-sites. In V_3Ga, the A15 structure phase extends [21] from 18% to 32% Ga, with however the highest T_c (14.5–15 K) at the stoichiometric 25% composition and a sharp fall off in T_c (approximately a factor of two for a change in Ga composition of ±5%) away from this 3:1 stoichiometry [21]. The history of the efforts to increase T_c in the A15's after superconductivity in V_3Si and Nb_3Sn was discovered in 1954 is essentially a history of struggling to achieve the proper 3:1 stoichiometry in compounds where the A15 structure was not stable there, i.e. in Nb_3Ga, Nb_3Ge, and Nb_3Si. Matthias et al., in their early work on Nb_3Ge, stated [22] "It is always the stoichiometric [A15] compound which has the maximum transition temperature." (As will be discussed in Section 2.2 (theoretical understanding) lattice disorder – including mixing atoms on a particular sublattice – strongly affects the electronic density of states and thereby T_c).

The two highest known T_c metallic A15's, Nb_3Ga and Nb_3Ge, will now be discussed to illustrate the difficulty achieving 3:1 stoichiometry and the maximum T_c, with 13 years being required to attain optimal T_c in Nb_3Ga and 17 years required in the case of Nb_3Ge, which is unstable in bulk form and was finally stabilized at 3:1 in the A15 structure in thin film form by sputtering.

Matthias and co-workers reported [23] T_c = 14.5 K for nominal Nb_3Ga, a_0 = 5.171 Å, in 1958, with no special effort given to determine the actual stoichiometry. Webb et al. [12] in 1971 succeeded (after great effort) is preparing essentially stoichiometric Nb_3Ga, T_c = 20.3 K, (the first reported binary compound with T_c > 20 K) with the lowest lattice parameter ever reported for this compound, 5.165 Å. They found a monotonic rise of T_c in Nb_3Ga with decreasing lattice constant, a_0, where the smaller a_0 is simply a metric for the approach to the perfect 3:1 stoichiometry. This point (that the T_c increase is due to the approach to unbroken chains of A-atoms and is not caused by the decrease in interatomic spacing) is made clear by the measurement [12] of a *depression* of the superconducting T_c in the T_c = 14.5 K Nb_3Ga material under pressure. See Ref. [24] for an overview on work on Nb_3Ga, where T_c was eventually increased to 20.7 K.

The success of Gavaler to achieve stoichiometric Nb_3Ge and T_c's approaching 23 K was the culmination of a community wide effort based on well-established trends of T_c values in the A15's with lattice constants. It was known that T_c was inversely proportional to lattice parameter in a given A15 family like Nb_3B where B is isoelectronic, i.e. in the same column in the periodic table. For example, B = In, a_0 = 5.303 Å, T_c = 9.2 K; B = Al, a_0 = 5.182 Å, T_c = 18.8 K; B = Ga, a_0 = 5.165 Å, T_c = 20.7 K. T_c is also $\propto 1/a_0$ within a specific compound like Nb_3Ga or V_3Ga where T_c has been studied as a function of lattice parameter. Thus, since the ionic radius of Ge (1.37 Å) is much smaller than that of Sn (1.62 Å), the expectation was that T_c for Nb_3Ge would be significantly larger than the 18.05 K T_c for Nb_3Sn. (The search for even higher T_c in A15 Nb_3Si, where the ionic radius for Si is 1.32 Å, is discussed below in Section 2.4).

The efforts to achieve higher T_c in Nb_3Ge started rather humbly. Carpenter and Searcy [25] reported a_0 = 5.168 ± 0.002 Å in 1956 for 'Nb_3Ge', and T_c was reported [26] to be 6.90 K in 1963. From there,