Physica C 514 (2015) 59–76

Contents lists available at ScienceDirect

Physica C

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

Superconductivity in the metallic elements at high pressures

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ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form 12 February 2015
Accepted 15 February 2015
Available online 24 February 2015

Keywords:
Superconductivity
High pressure
Periodic table

ABSTRACT

Although the highest superconducting critical temperature, T_c, found in an elemental solid at ambient pressure is 9.2 K (niobium), under the application of ultra-high pressures, several elements exhibit T_c values near or above 20 K. This review includes a survey of the occurrence and understanding of pressure-induced superconductivity in the subset of elements that are metallic at ambient pressure. A particular focus is directed towards those elements that display the highest superconducting critical temperatures or exhibit substantial increases in T_c with pressure. A separate article in this issue by Shimizu will cover pressure-induced superconductivity in elements that are insulating at ambient pressure.

Contents

1. Introduction

The importance of high pressure studies to our understanding of condensed matter was summarized succinctly by P.W. Bridgman, who was awarded the 1946 Nobel Prize in Physics for his pioneering work in high pressure:

> The condensed state, *par excellence*, is obviously presented by matter under high pressure, so that, to say the least, our understanding of the condensed state cannot be regarded as satisfactory until we can give an account of the effect of pressure on every variety of physical phenomena.
>
> – P.W. Bridgman (1935) [1].

In the case of superconductivity, efforts to give an account of the effects of pressure on T_c have stimulated numerous insights into the conditions that are most favorable for superconductivity.

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http://dx.doi.org/10.1016/j.physc.2015.02.032
0921-4534/

With the extension of accessible pressures into the megabar range, made possible by the advent of diamond anvil cells, pressure has become an even more valuable tool in that relatively enormous changes in energy can be brought about. For example, the change in free energy ($\int PdV$) resulting from compression to 100 GPa (1 megabar) can be on the order of hundreds of meV per atom or more. This is a large change compared to that obtained by cooling a material to low temperature (300 K $\sim$ 25 meV) or applying high magnetic fields (1 $\mu_B \times 100$ tesla $\sim$ 6 meV).

The study of pressure effects on elemental superconductors dates back almost as far as the discovery of superconductivity itself, with the first such study being performed in the laboratory of Kammerling Onnes in 1925 [6]. In that study, elemental tin was subjected to a modest pressure of roughly 300 bars and a small (5 mK) suppression of the superconducting critical temperature was observed. High pressure technology has since advanced tremendously, and it now is possible to subject matter to static pressures on the order of 300 GPa or more.

Historically, experiments near the limits of achievable pressure have focused to a large extent on pure elemental solids. As the elemental solids have been studied at ever increasing pressures many elements that are not superconducting at ambient pressure have been found to be superconducting at high pressure and the T_c values of some elements has been found to increase dramatically under pressure. Though superficially the simplest of condensed matter systems, the elements exhibit surprising complexity when subjected to extreme compression. One of the exciting developments of the last two decades is that several elements have been found to become superconducting at temperatures near or above 20 K. The elements with the highest superconducting transition temperatures include Li ($T_c \approx 15$–20 K at 30 GPa [7–9]), Ca ($T_c \approx 21$–29 K at 220 GPa [10]), Sc [11] and Y [12] ($T_c \approx 20$ K near 100 GPa), V ($T_c \approx 17$ K at 120 GPa [13,14]), and S ($T_c \approx 17$ K at 220 GPa [15]). These transition temperatures in pure elemental solids are especially remarkable considering the decades of research that went into developing the first superconducting *compound* with a T_c of 20 K [16].

Fig. 1 presents an overview of the occurrence of superconductivity throughout the periodic table. At ambient pressure, 29 elements are superconducting (orange[1] boxes). Under the application of sufficiently high pressures, another 24 elements become superconducting (blue boxes). Several elements that are magnetic at ambient pressure (green boxes) have been found to become superconducting under pressure. A number of the pressure-induced superconductors are elements that are insulating at ambient pressure and only become superconducting after being driven metallic. Thus, at present, the majority of the stable elements in the periodic table can be driven superconducting at sufficiently low temperatures and high pressures.

This aim of this article is to provide an overview of the occurrence and present understanding of superconductivity in the elemental solids that are metallic at ambient pressure. A separate contribution to this issue by Shimizu will cover pressure effects in elements that are insulating at ambient pressure and become superconducting following pressure-induced metallization. Another separate contribution by Struzhkin is covers the fascinating possibility of pressure-induced superconductivity in elemental hydrogen. In an article of this length it is impossible to exhaustively cover pressure effects on superconductivity even in the subset of metallic elemental solids. We focus, therefore, on those elements that exhibit the highest T_c values, show a substantial increases in T_c with pressure, or exhibit an interplay between superconductivity and other phases. Where possible, trends within various families of elements are highlighted and the prospects for inducing superconductivity in some as-yet non-superconducting elements are discussed. In preparing this work, a number of related reviews were helpful. Buzea and Robbie [17] have provided a useful systematic overview of superconductivity across the entire periodic table that includes plots of the pressure dependence of T_c for most of the elements. Other reviews have covered various subsets of the pressure-induced superconducting elements [18–20,2,21–23,2].

1.1. Experimental constraints

Superconductivity at temperatures above 15 K in the elemental solids only occurs for pressures of several tens of GPa or higher. Reaching these pressures in combination with low temperatures is achieved using diamond anvil cells [24]. The technical challenges associated with the use of diamond cells place severe constraints on the types of measurements that can be performed. Direct probes of the occurrence of superconductivity at these pressures are typically limited to electrical resistivity and ac magnetic susceptibility [25] (or variations of the ac susceptibility technique [15]). Other types of measurements that are typically used to build a more detailed understanding of the nature of the superconducting state, such as *e.g.*, specific heat, photo-emission spectroscopy, tunneling, and nuclear magnetic resonance, to name a few, are either impractical or impossible for measurements at very high pressures.

On the other hand, 3rd generation synchrotron sources, with their intense, monochromatic, and highly focused X-ray beams, have created a revolution in high pressure structure determination [26]. The structures of many of the elemental solids have been accurately determined from low pressure all the way into the megabar range [27,28]. The extent of the progress in high pressure X-ray science is well represented by the case of sodium, where a structure containing over *five hundred* atoms per unit cell was solved by carrying out measurements on a single crystal at a pressure of nearly 120 GPa [29]. Synchrotron absorption spectroscopy using polarized X-rays is also allowing magnetic properties to be probed to very high pressures in some cases [30]. Inelastic X-ray scattering techniques have been used to map the phonon-spectra of some elements at elevated pressures [31,32]. However, although there exists a great deal of data on the ambient pressure properties of the elemental solids, at very high pressures, in many cases little more than T_c and crystal structures are known. This situation has created a fertile and challenging testing ground for theoretical efforts to reproduce the observed T_c values, to explain their origins, and to offer insights into where higher critical temperatures might be sought.

2. Simple metals

So called simple-metals (*sp*-electron metals) have electronic structures that are well described by the free-electron model. In simple metals that exhibit superconductivity at ambient pressure, T_c consistently goes down upon an initial increase of pressure. This behavior is observed in Zn, Cd, Hg, Al, Ga, In, Sn, and Pb (see References [17,2] and references therein). The effect of increasing pressure is to reduce the average distance between the atoms. In the most basic picture, this leads to band broadening. In metals this tends to produce a lowering of the density of states at the Fermi-level, $N(E_F)$. Although a variety of effects can lead to deviation from this behavior, for simple (*sp*-electron) metals at low to moderate pressures this basic picture hold true. A second tendency of pressure is to cause the lattice to stiffen, *i.e.*, the spring constant, κ,

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.