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Studies in superconductivity at extreme pressures

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Abstract

High pressure studies have played an important role in the field of superconductivity since the first experiments by Sizoo and Onnes in Leiden in 1925. A rapid dependence of the transition temperature on pressure signals that the material is capable of higher values of T_c at ambient pressure. Significant extensions of the pressure range, most recently to pressures above 1 Mbar using the diamond-anvil cell, have resulted in the discovery of many new superconductors. The transition temperature of Y metal has very recently been pushed by 1.15 Mbar pressure to 20 K, a value for an elemental superconductor second only to that of Ca at Mbar pressures. Such enormous pressures are even sufficient to destroy the free-electron character of the conduction electrons in the alkali metals. Selected experiments are discussed which illustrate these features.

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High pressure experiments play an important role in the field of superconductivity in three primary ways, namely by: (a) increasing the number of known superconductors and enhancing their transition temperatures T_c to record values, (b) serving as a guide in the synthesis of materials with superior superconducting properties at ambient pressure, and (c) giving information on the pairing interaction and allowing quantitative tests of theory [1]. In this paper we focus on the first of these roles.

Across the periodic table there are 29 elemental metals which superconduct at ambient pressure, as seen in Fig. 1. The significant extension of the pressure range to nearly 20 GPa (1 GPa = 10 kbar) by Wittig in the 1960s led him to discover 12 additional elements which only superconduct under high pressure. In recent years the search for new superconductors has been extended into the Mbar pressure range using diamond-anvil-cell technology. Altogether there are 23 high-pressure superconductors, as seen in Fig. 1. There are thus a total of 52 superconducting elements in the periodic table. Some of the elemental solids, like B, O, Si, S, and I_2 are normally insulators or semiconductors and require high pressure to transform them into metals. Others, like Li, Sc, Fe, Y, Cs, Ce, and Lu, are metallic but require high pressures to make them superconduct. In Fe and Ce superconductivity appears only after high pressure has squeezed out their magnetism. It has been proposed that all nonmagnetic materials may become superconducting at sufficiently high pressures [2].

A glance at Fig. 1 reveals that the transition metals are far and away the class of elements with the highest "superconductivity success rate". In fact, with the sole exception of Sc, Y, Pd, and Pt, all nonmagnetic transition metals are superconducting at ambient pressure (note that Pd and Pt are *almost* ferromagnetic). So why do not Sc and Y superconduct? Apparently, being the first transition metals in the 3d and 4d series, respectively, they simply do not have a sufficient number of d electrons. Due to the well known phenomenon of s → d transfer, the d-electron occupancy n_d increases under pressure, thus inducing superconductivity if the pressure is sufficiently high. The d-electron

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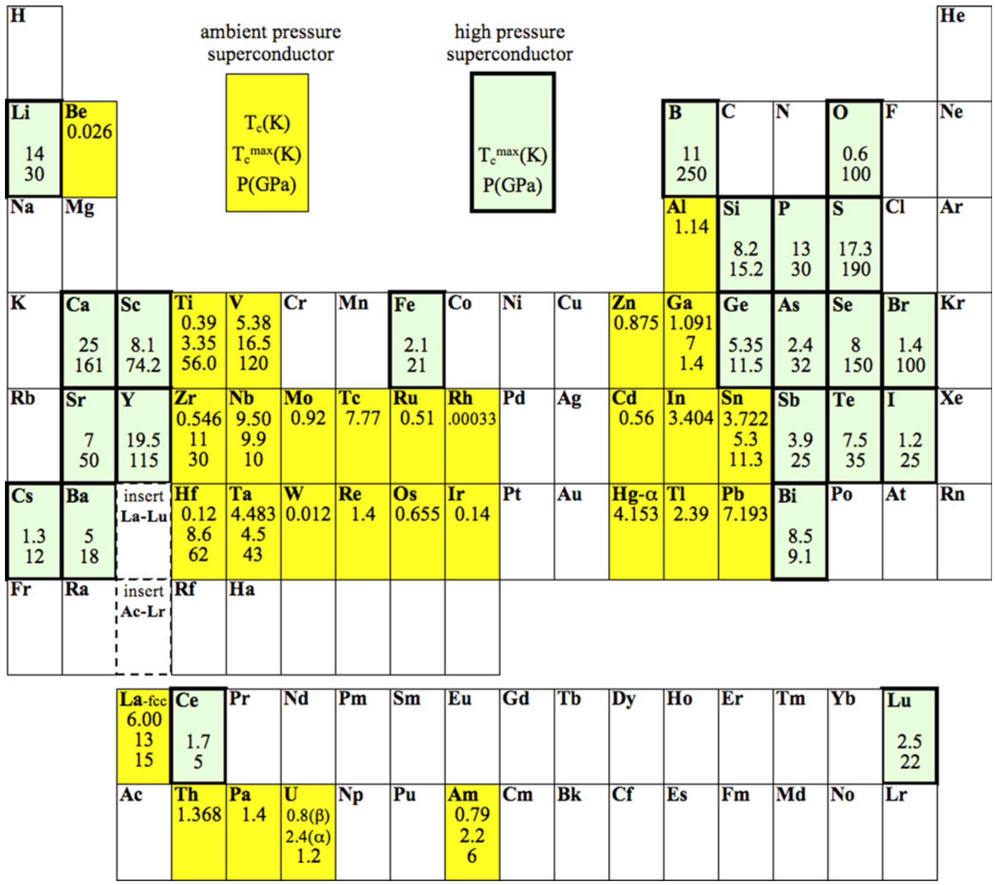

Fig. 1. Periodic table listing 29 elements which superconduct at ambient pressure (yellow) and 23 elements which only superconduct under high pressure (green with bold lines). For each element the upper number gives the value of T_c (K) at ambient pressure; the middle number gives maximum value T_c^{max} (K) in a high-pressure experiment at P (GPa) (lower number). Figure taken from Ref. [1] which contains full references and details. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

occupancy n_d has been shown to be the single most important factor determining the crystal structures for the 3d, 4d, and 5d transition metals [3] as well as for the members of the rare-earth series [4] which, in their trivalent state, have the same electron configuration as the beginning transition metal La in the 5d series. The relevance of the value of n_d for the appearance of superconductivity will be examined below.

Superconductivity in Y [5] and Sc [6] was discovered under high pressure by Wittig; the transition temperature T_c rose higher for Y, reaching 9 K at 30 GPa [7]. As seen in Figs. 1 and 2, very recent ac susceptibility experiments on Y to 1.15 Mbar show that T_c goes as high as 19.5 K (susceptibility midpoint) [8] with the susceptibility onset at 20 K, second only to the record value $T_c \simeq 25$ K for Ca very recently reported by Shimizu et al. [9] from the resistivity onset. In contrast to La and S, however, T_c for Y is seen in Fig. 2 to increase monotonically with pressure; in fact, the dependence of T_c on the relative sample volume V/V_o is nearly linear [8]. Also shown in Fig. 2 are the pressure dependences of T_c for those non-alkali elemental superconductors where T_c reaches the highest values. In fact, for the elements Ca, Y, Lu, Sc, V, B, and P, T_c is still climbing at the highest pressures shown.

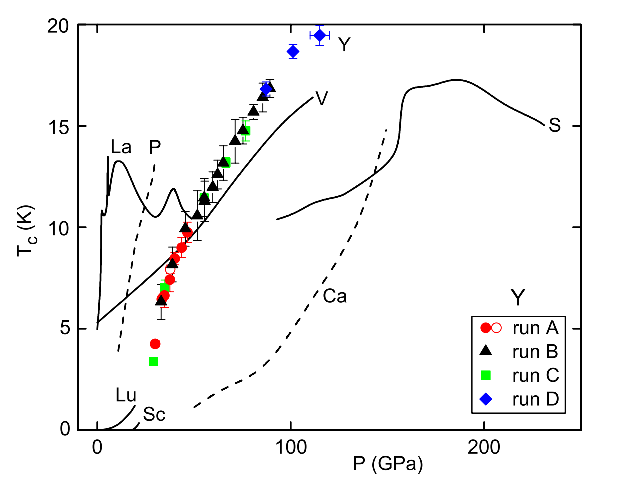

Fig. 2. Pressure dependence of T_c for those non-alkali elements with the highest values of T_c under pressure. Figure taken from Ref. [1]. The very recent results for Ca from Ref. [9] are not included.

More than 30 years ago Johansson and Rosengren [10] pointed out that the ratio of the Wigner–Seitz radius to the ion core radius, r_a/r_c, is a measure of the free volume available to the conduction electrons; on the other hand, in a transition metal system the d-electron occupancy n_d

is an inverse function of the ratio r_a/r_c. Under pressure, the ratio r_a/r_c decreases (n_d increases) since under compression r_a decreases with the atomic volume, $V_a \equiv \frac{4}{3}\pi r_a^3$, and r_c remains relatively constant. These authors also pointed out a correlation between the superconducting transition temperature T_c and the value of the ratio r_a/r_c for Y, La, Lu, and La–Y and La–Lu alloys [10]. In Fig. 3 we plot T_c versus r_a/r_c for the trivalent transition metals La, Y, Lu and Sc. The correlation is evident. The value of T_c for these four elementary superconductors only rises above 1 K if r_a/r_c falls below 2.1. For La, which superconducts at 6 K at ambient pressure, the initial value of r_a/r_c is seen to lie just below 2.1, whereas progressively higher pressures are required to lower r_a/r_c sufficiently that Y, Sc, and Lu become superconducting. Aside from an initial increase in T_c with pressure, the $T_c(P)$ dependences for La and Y are quite different.

In contrast to the transition metals, where an increase in T_c with pressure is not uncommon, in simple s, p-metal superconductors like Sn, In, Pb, and Al one would expect, and one finds, that T_c always *decreases* under pressure [1]. The reason for this is evident for BCS (electron–phonon) superconductors: increasing lattice stiffening under pressure coupled with a mild decrease in the electronic density of states (for a 3D free-electron gas $N(E_f) \propto V_a^{2/3}$) leads to a reduction in the strength of the electron–phonon coupling λ, i.e. T_c decreases [1]. From this it follows immediately that a simple metal which does *not* superconduct at ambient pressure should *never* become superconducting under pressure. All alkali metals fit into this category since they have only a single s-electron in the conduction band and none are known to superconduct at ambient pressure (no superconductivity was found in Li metal down to 100 μK [12]!). So why is it that both Cs [5,13] and Li [9,14–16] become good superconductors under pressure (see $T_c(P)$ for Li in Fig. 4)? Because in all alkali metals under sufficiently high pressures the conduction electrons lose their nearly-free-electron character [11]. In Cs the bottom of the 5d-band drops below the Fermi energy for pressures above 3 GPa, initiating a s → d transfer which is complete near 15 GPa. At the pressure (~12 GPa) where superconductivity first appears, Cs is thus no longer a simple metal but has become a transition metal. As we pointed out above, in transition metals superconductivity is the rule rather than the exception.

But why does Li become superconducting under pressure? In Li the 3d band is located far above the Fermi energy so that s → d transfer does not occur. Boettger and Trickey [17] pointed out many years ago that the electronic structure of Li under sufficient pressure deviates strongly from that of free electrons, the bands near the Fermi energy actually becoming narrower, a counterintuitive result. More recently, Neaton and Ashcroft have found marked anomalies in the electronic structure in Li [18] and Na [19] at elevated pressures with possible superconductivity and have predicted cation pairing at pressures near 1 Mbar accompanied by a transition to semiconducting behavior.

How can such canonical free-electron systems as the alkali metals with their nearly spherical Fermi surfaces show such anomalous behavior under pressure? In the simple free-electron picture both the Fermi wavevector k_f and the Brillouin zone boundaries increase under compression at the same rate, namely with the inverse first power of the lattice parameter a, so the Fermi surfaces remain spherical. However, in real metals the conduction electrons are not free to wander *throughout* the crystal lattice but, because of the Pauli exclusion principle and wavefunction orthogonality [18], must stay out of the atomic core region. The ion pseudopotential seen by the conduction electrons grows much larger as the electron de Broglie wavelength becomes comparable with the dimensions of the interstitial

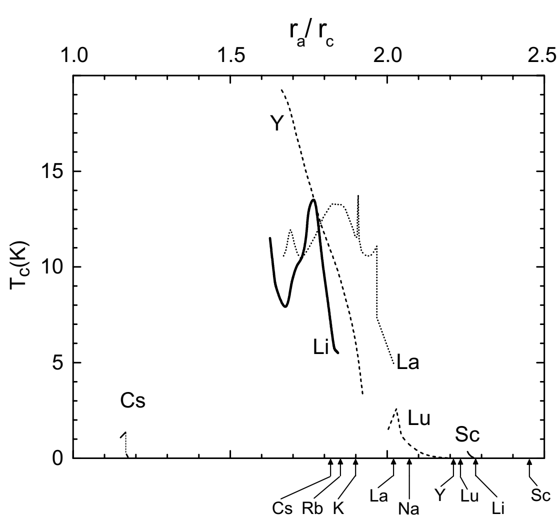

Fig. 3. Value of T_c versus ratio of Wigner–Seitz to ionic radii, r_a/r_c, for Y, Sc, La, Lu, Li, and Cs. The values of this ratio at ambient pressure are indicated by the vertical arrows at the bottom of the figure. Figure taken from Ref. [11].

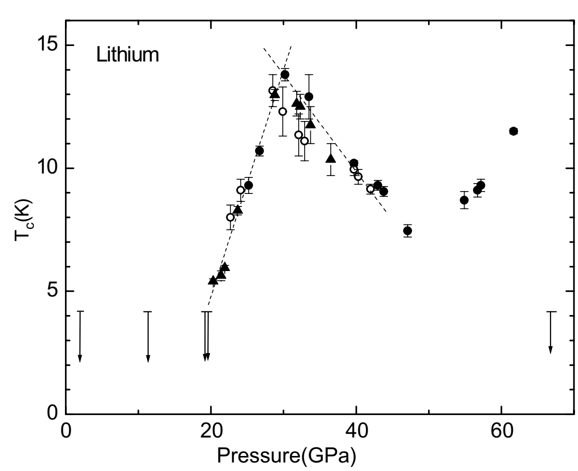

Fig. 4. Superconducting transition temperature T_c of Li versus nearly hydrostatic pressure; figure taken from Deemyad et al. [16].

regions to which the conduction electrons are confined. A recent *ab initio* electronic structure calculation finds that Li's Fermi surface contacts the zone boundary already at ~8 GPa and at somewhat higher pressures takes on the appearance of the connected Fermi surface of Cu metal [20]. At pressures above 20 GPa, Li is anything but a simple metal!

From the above discussion it would follow that the deviations from nearly-free-electron behavior and the possibility of superconductivity would be strongly enhanced when the free volume available to the conduction electrons falls below a certain percentage of the total volume, or, equivalently, when the ratio r_a/r_c falls below a critical value. In Fig. 3 we include a plot of T_c versus r_a/r_c for Li and Cs. We see that the T_c dependence for Li follows rather closely the correlations exhibited by the trivalent transition metals. However, the superconductivity in Cs only appears at a much *lower* value of r_a/r_c, demonstrating once again that "life is not so simple" with the alkali metals. Unlike the transition metals, the changes experienced by the highly compressible alkali metals under pressure are drastic in nature and require more than one parameter for an adequate description. Whereas superconductivity is believed to first appear under pressure in the fcc phase in Li, superconductivity in the heavy alkali metal Cs first appears after the transition from fcc to the tetragonal and orthorhombic phases [11].

From the above discussion it would appear likely that at sufficient pressures all alkali metals will become superconducting. Shi and Papaconstantopoulos [21] have predicted superconductivity at high pressures for Li, K, Rb, and Cs in the 5–10 K range, but at much lower temperatures for Na. To date, Na, K, and Rb have not been found to superconduct [11]. The search for superconductivity in the alkali metals and their alloys remains a fruitful area for future experimentation.

Acknowledgement

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