Superconductivity in Sc metal and Li(Mg) alloy under extreme pressure

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Abstract

Li and Sc are two of the 23 elements which only superconduct under high pressure. In previous studies $T_c$ for Li reaches 14 K at 30 GPa, but for Sc only 0.35 K at 21 GPa. We determined $T_c(P)$ for Sc to be 74.2 GPa and found that $T_c$ increases monotonically with pressure to 8.2 K. Changes in the superconducting phase diagram of monovalent Li are studied upon alloying with 10% divalent Mg.

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At ambient pressure there are 29 known superconducting elements in the periodic table of which 19 are metals with d-electron character near the Fermi energy (Ti, V, Zr, Nb, Mo, Tc, Ru, Rh, La, Hf, Ta, W, Re, Os, It, Th, Pa, U, Am) and 10 are metals with s,p-electron character (Be, Al, Zn, Ga, Cd, In, Sn, Hg, Tl, Pb) [1]. Superconductivity is never found in insulators or semiconductors (e.g. Si, Ge, or O$_2$) and usually not in magnetic materials (e.g. Fe, Ce); yet these five elements all become superconducting under sufficient pressure either because they experience an insulator-to-metal transition or their magnetism is suppressed.

Nevertheless, not all nonmagnetic metals superconduct at ambient pressure, in particular, none of the monovalent s,p-electron elements (alkali and noble metals) nor the trivalent d-electron metals Sc (the lightest transition metal), Y, and Lu. Would one expect these elements to become superconducting under pressure? In the case of the alkali and noble metals, certainly not! The reason is that the superconducting state in all known simple metal (s,p-electron) superconductors is weakened under pressure, i.e. $T_c$ decreases [1,2]. It follows immediately that a nonsuperconducting simple metal should never become superconducting under pressure. And yet, it is well known that both Cs and Li are high-pressure superconductors [2].

In Fig. 1 it is seen for Li that $T_c(P)$, following an initial rapid rise, exhibits quite complex behavior likely originating from structural phase transitions.

So why does a canonical free-electron metal like Li become superconducting under pressure? The answer lies in an important paper by Neaton and Ashcroft in 1999 [5] which shows that, if Li’s ion cores are brought close together through high compression, its conduction electrons are forced to reside in the ever smaller interstitial regions outside the ion cores and thus lose their free-electron character, taking on some p- and d-character. In fact, under extreme pressure Li’s conduction bandwidth actually decreases and its Fermi surface morphs from a nearly perfect sphere to one highly connected like that of Cu [6].

Another method to add complexity to the electronic structure of Li would be to increase the electron density by alloying monovalent Li with divalent Mg, thus forcing the Fermi surface to contact the Brillouin zone at ambient pressure. This may have an influence on the critical pressure for the structural transition to fcc [7] which is believed to accompany the onset of superconductivity [2]. Although the data in Fig. 1 do not extend to low enough temperatures to allow a reliable estimate of this critical pressure, the slope $dT_c/dP$ is seen to be considerably less for the alloy [4]. Future X-ray diffraction studies should help clarify the relationship between crystal structure and superconductivity. Further ac susceptibility experiments on

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Li(Mg) alloys with higher Mg concentrations are underway. A further way to increase the complexity of the electronic structure for a free-electron metal would be to add d-electrons to the conduction band near the Fermi energy. Indeed, as pointed out above, nonmagnetic d-electron metals have a high success rate for superconductivity. Nevertheless, of the trivalent d-electron metals, Sc, Y, La, and Lu, only La is superconducting at ambient pressure. This is likely related to the fact that La has more d-electrons in its conduction band due to its relatively large ion core [8].

Many years ago Wittig demonstrated that Sc, Y, and Lu become superconducting under pressure [9]. In a recent paper [10] we extended the earlier work on Y to much higher pressures, obtaining a strong monotonic increase in $T_c$ to 20 K at 115 GPa (1.15 Mbar). Here, we report parallel experiments on Sc where, as seen in Fig. 2, $T_c$ increases to 8.2 K at 74 GPa [13]. It seems likely that the strong initial increase in $T_c$ under pressure seen in Fig. 2 for these four trivalent d-electron metals is correlated with an increase in the d-electron occupancy $n_d$ caused by pressure-induced s → d transfer, a well-known and general phenomena in metallic systems [8,15]. An attempt to correlate $T_c$ for Sc, Y, La, and Lu with the relative size of the interstitial regions achieved only limited success [13]. Perhaps a stronger correlation exists between $T_c$ and $n_d$; a meaningful test of this possible correlation will require the extension of previous experimental and theoretical work. Parallel measurements of $T_c(P)$ are underway on Lu and Sc metal to Mbar pressures as a further step in this direction.

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References