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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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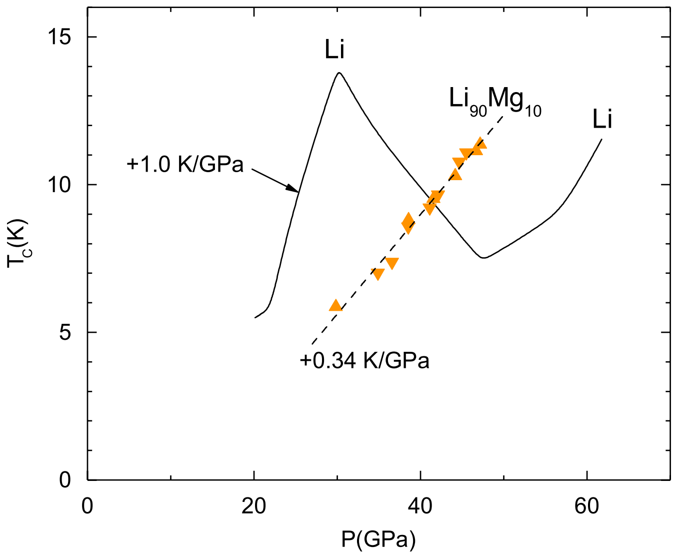

Fig. 1. Superconducting transition temperature T_c versus pressure for pure Li (solid line) [3] and $Li_{90}Mg_{10}$ alloy [4] ((▲) increasing, (▼) decreasing pressure). Values of initial slope dT_c/dP are given.

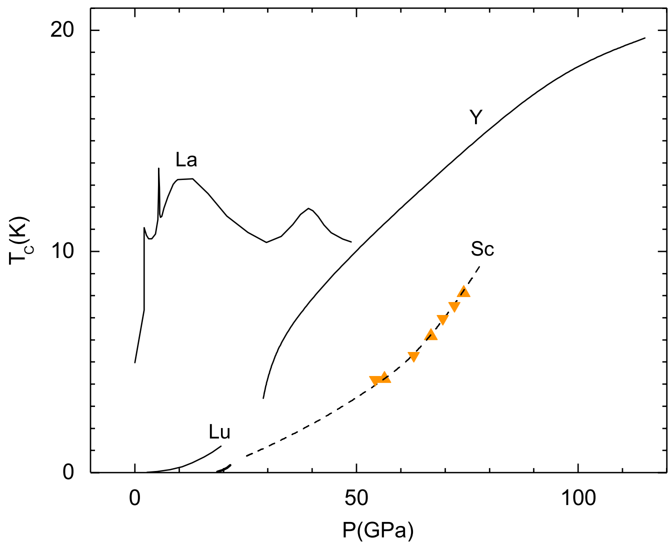

Fig. 2. Superconducting transition temperature T_c versus pressure for La [11], Lu [12], Y [10] (solid lines). Dashed line for Sc is a guide to the eye and links recent data ((▲) increasing, (▼) decreasing pressure) from Ref. [13] to previous results of Wittig et al. [14] to 21.5 GPa (short solid line).

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 $\rightarrow$ 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

[1] See, for example, J.S. Schilling in: J.R. Schrieffer (Ed.), J.S. Brooks (Assoc. Ed.), Handbook of High Temperature Superconductivity: Theory and Experiment, Springer, Hamburg, 2007, and references therein. Preprint arXiv: cond-mat/0604090.
[2] For a review, see: J.S. Schilling, High Pressure Res. 26 (2006) 145, and references therein.
[3] S. Deemyad, J.S. Schilling, Phys. Rev. Lett. 91 (2003) 167001.
[4] J.J. Hamlin, M. Debessai, J.S. Schilling, unpublished.
[5] J.B. Neaton, N.W. Ashcroft, Nature 400 (1999) 141.
[6] A. Rodriguez-Prieto, A. Bergara, V.M. Silkin, P.M. Echenique, Phys. Rev. B 74 (2006) 172104.
[7] M. Hanfland, K. Syassen, N.E. Christensen, D.L. Novikov, Nature 408 (2000) 174.
[8] J.C. Duthie, D.G. Pettifor, Phys. Rev. Lett. 38 (1977) 564.
[9] For a review, see: C. Probst, J. Wittig, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 1, North-Holland, Amsterdam, 1978, p. 749 (Chapter 10).
[10] J.J. Hamlin, V.G. Tissen, J.S. Schilling, Phys. Rev. B 73 (2006) 094522;
J.J. Hamlin, V.G. Tissen, J.S. Schilling, Physica C 451 (2007) 82.
[11] V.G. Tissen, E.G. Ponyatovskii, M.V. Nefedova, F. Porsch, W.B. Holzapfel, Phys. Rev. B 53 (1996) 8238.
[12] J. Wittig, Mater. Res. Soc. Sympos. Proc. 22 (1984) 17.
[13] J.J. Hamlin, J.S. Schilling, Phys. Rev. B 76 (2007) 012505.
[14] J. Wittig, C. Probst, F.A. Schmidt, K.A. Gschneidner Jr., Phys. Rev. Lett. 42 (1979) 469.
[15] D.G. Pettifor, J. Phys. F 7 (1977) 613.