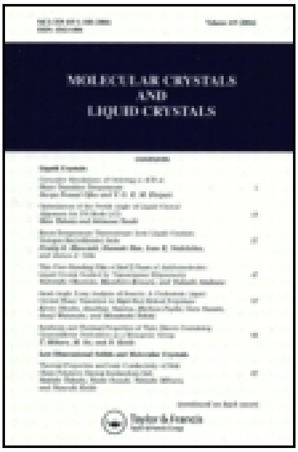

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THE ROLE OF PRESSURE IN THE STUDY OF ORGANIC SUPERCONDUCTORS

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Abstract The impact of high pressure in the study of organic superconductivity is reviewed. Studies of the pressure dependence of the superconducting transition temperature of the $(ET)_nX_m$ family using solid He pressure techniques and high quality single crystal samples are discussed in detail.

INTRODUCTION

Pressure has been extremely important in the study of organic superconductors beginning with the report of Jerome, Bechgaard and coworkers[1] of the first organic superconductor at pressures above 9 kbar. This initial discovery of a superconductor $(TMTSF)_2PF_6$ with a maximum T_c of 1.6K at a pressure of 6.3 kbar prompted studies in many laboratories which have resulted thus far in about thirty organic superconductors including materials with superconducting transitions above 10K at ambient pressure.[2] This order of magnitude improvement in a decade has involved a variety of synthesis breakthroughs aided by insights given by the pressure studies of the various materials.

It is convenient, as in Brossard et al,[3] to classify the organic superconductors into five families. The first family is the Bechgaard salts consisting of the TMTSF (tetramethyl-tetraselenafulvalene) cation and closed shell anions.[4] The above mentioned first organic superconductor $(TMTSF)_2PF_6$ is a much studied example. The second family is the $(BEDT\text{-}TTF)_nX_m$ series[5] (where (BEDT-TTF)=(ET)=bis-(ethylenedithio) tetrathiofulvalene) which at present has the record high T_c of ~10K with $X = Cu(SCN)_2$ and $n = 2$, $m = 1$. The third family is $(DMET)_2X$ (where unsymmetric DMET = dimethyl (ethylenedithio)-diselenadithiafulvalene) with $X = I_3$, I_2Br, IBr_2, $Au(CN)_2$, AuI_2, $AuBr_2$, and $AuCl_2$. The unsymmetric donor is a hybrid[6] of TMTSF and BEDT-TTF with a low T_c ~0.5K. The fourth family is characterized[7] by $(MDT\text{-}TTF)_2\ AuI_2$ (where (MDT-TTF = methylenedithio tetrathiafulvalene) which also has an unymmetric donor as does the third family, but has a $T_c = 4.5K$. The fifth family is based on the $D(M(dmit)_2)_n$ compounds[3] which are composed of organo-sulfur donors D or tetramethylammonium cations[8] and acceptor metal M(dmit) complexes (dmit = 1,3-dithia-2-thrione-4, 5 dithiolato). Superconductivity has been observed under ~ 20 kbar pressure near 5K for M = Pd in $TTF(Pd(dmit)_2)_2$. For M = Ni this material is superconducting with an unusual positive pressure derivative between 1.1K and 1.6K for pressures of 2 to 7 kbar respectively.[9]

The typical organic superconductors are extremely anisotropic and at low temperatures all pressure media are of necessity solid. This has resulted in considerable disagreement in results from various laboratories and some continuing controversy. In this discussion, results on a relatively large spectrum of organic materials will be compared where all have been studied using the same experimental system described below in which single crystal samples and hydrostatic conditions were employed. This eliminates concern with different pressure techniques and allows a direct comparison of the properties of the materials.

EXPERIMENTAL

The materials discussed in this report were all single crystals. Details of sample synthesis are given elsewhere.[5]

Historically, pressure studies of superconductivity seemed to be very tolerant of the pressure technique because most materials were polycrystalline with fairly high symmetry structures. Indeed Chester and Jones[10] literally used a c-clamp and obtained essentially the correct results on simple type I superconductors. The organic superconductors are, in contrast, usually very delicate, highly anisotropic single crystals so hydrostatic conditions are desirable and, in many cases, necessary. The solid He pressure technique[11] has been demonstrated to provide effectively hydrostatic conditions for a variety of microscopic measurements such as NMR, ESR, magneto-optic and transport measurements for pressures up to about 10 kbar.

Briefly, this technique involves careful isobaric freezing of He around the sample. In a manner similar to Bridgman growth the experiment is lowered slowly into the temperature gradient above a liquid He bath. The temperature is monitored with a thermocouple during this process. Below the freezing point of He^4, the cooling is assumed to be at a constant volume so the final pressure is calculated from the known phase diagram of He^4. Absolute values of the pressure are better than ± 5% but values can be reproduced to better than ± 2%.

Superconducting transition temperatures discussed here were determined using an rf impedance technique[12] in which the single crystal samples were slipped into custom wound rf coils (typically 0.025 mm diameter wire). The onset of this signature closely mimics the onset of diamagnetism as observed in a SQUID magnetometer on the same samples. The temperature determination is made using a carbon glass resistance thermometer thermally anchored to the outside of the pressure vessel immediately adjacent to the crystal sample location. The calibration of the thermometer is checked regularly against the vapor pressure of He^4 below 4.0K and against known superconducting transition temperatures in the 4-10K range.

RESULTS AND DISCUSSION

As noted at the onset, we are confining our comparison of pressure results primarily to those obtained in solid He because of the difficulties sometimes experienced with less hydrostatic media. The best family of organic superconductors for comparison is necessarily the $(BEDT\text{-}TTF)_nX_m$ system because of the relatively large number of members identified to date. Since the initial report[13] of superconductivity above 6 kbar in $(ET)_2ReO_4$ a large number of $(ET)_nX_m$ material[5] have been shown to be superconductors. These include[14] $(ET)_2X$ where X = I_3, IBr_2, AuI_2 and $Cu(NCS)_2$ which superconduct at ambient pressure as does[15] $(ET)_3(I_3)_{2.5}$. $(ET)_3Cl_2(H_2O)_2$ has recently been shown[16] to superconduct at 16 kbar. Two Hg containing superconducting salts have been identified,[17,18] $(ET)_4Hg_3Cl_8$ and $(ET)_4Hg_{2.89}Br_8$ By contrast the $(TMTSF)_2X$ family of Bechgaard salts is fewer in number with lower values of superconducting transition temperature T_c. These materials are, nonetheless, extremely interesting because of the magnetic transitions first discovered[19] in solid He studies in $(TMTSF)_2PF_6$ (the first organic superconductor). We will not discuss these ongoing studies but limit this treatment to discussion of the pressure dependence of T_c itself. The pressure derivatives of T_c in the $(TMTSF)_2X$ materials[4,13] are negative and of the order of 10^{-1} K/kbar. There is a general agreement in the literature on this aspect of the pressure studies although the pressure at which $(TMTSF)_2PF_6$ first becomes superconducting varies considerably from the ~9 kbar first reported by Jerome et al[1] to the value of 6.3 kbar found in our studies[12] in solid He^4.

The third family $(DMET)_2X$ have low T_c values near 0.5K so that pressure studies of T_c are extremely difficult. The fourth family of $(MDT\text{-}TTF)_2AuI_2$ was studied using the solid He technique and gave[20] a negative pressure derivative of 0.92 K/kbar which as we shall see is the usual sign for the effect for the vast majority of organic superconductors.

The fifth family thus far exhibits superconductivity only under pressure. The Pd analogue shows a decrease in T_c with pressure above ~ 20 kbar[3] while the Ni analogue has an unusual increase in T_c with pressure.[9]

The $(ET)_2X$ series show a rather similar behavior for dT_c/dP over a large range of values for T_c from near 1K to 10K. Results for $X=I_3$(β and β*), AuI_2, IBr_2 and $Cu(NCS)_2$ are displayed in Fig. 1. The pressure derivatives are all negative and very large, greater than 1 K/kbar. The initial change of T_c for $(ET)_2Cu(NCS)_2$ is -3 K/kbar which is the largest reported value for dT_c/dP for any superconducting material to our knowledge.[21] These results are in qualitative agreement with measurements in other laboratories[22] using less hydrostatic pressure media. We attribute the quantitative disagreement to non-hydrostatic effects which are minimized in the solid He technique.

Disagreement persists[23,24] with respect to the phase diagram of $(ET)_2I_3$. With high quality single crystal samples and careful isobaric freezing of the He^4 pressure medium, we have never observed transformation from the low T_c(~ 1.5K) β phase to the high T_c (~8K) β* phase. However with too rapid freezing of the He, 8K superconductivity was occasionally observed. With a procedure discussed in detail in reference 25 where high pressure (0.5 to 2 kbar)Ar is

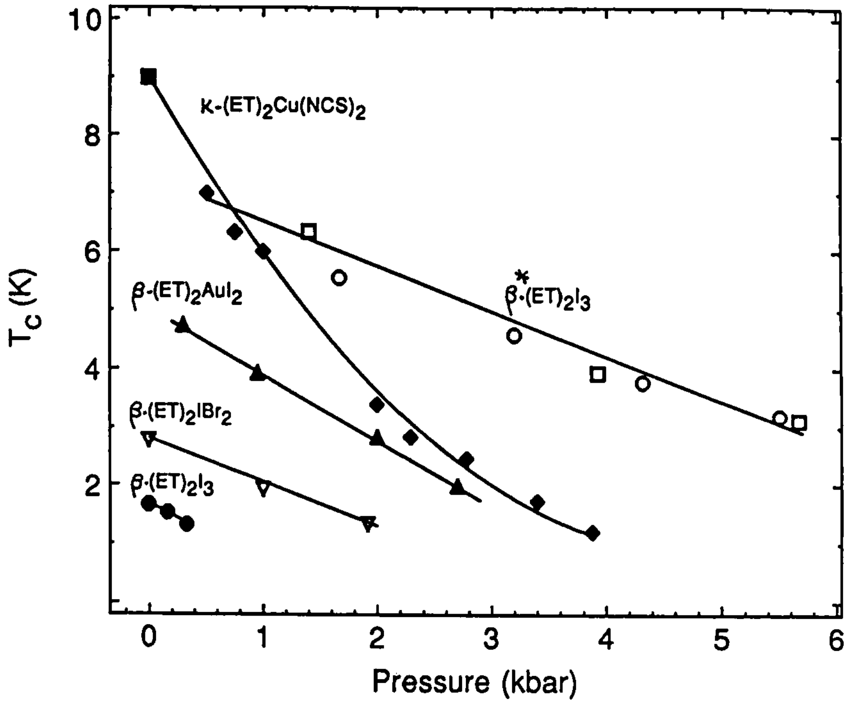

FIGURE 1 Comparison of T_c vs. pressure for superconducting members of the $(ET)_2X$ family.

rapidly frozen about the sample, the 8K phase could be accessed in a completely reproducible manner. The phase can be recovered at zero pressure by warming above the freezing point of the Ar and releasing the pressure, and is stable to 120K. We attribute this behavior to the requirement of a component of shear in order to effect the transition from β to $\beta*$ (at least on reasonable time scales). This shear could arise from electrical leads, differential thermal expansion between the sample and anything to which it might be attached or to non-hydrostatic (shear) components in the stress applied to the sample.

In Fig. 2 are results of recent studies[26] of $(ET)_4Hg_{2.89}Br_8$ which show conclusively that the ~ 4K superconductivity is not due to free Hg. This is often a concern in Hg containing materials when T_c is so close to that of elemental Hg. The large and non-monotonic dependence of T_c on pressure initially increasing at ~ 1 K/kbar and then decreasing above ~ 4 kbar after achieving a maximum value of 6.7K, is anomalous, particularly for the $(ET)_nX_m$ family. All other members have large negative derivatives as evident from Fig. 1. To date, there is no structural data collected under pressure but it is likely that a rather reversible phase transition occurs near 4 kbar.

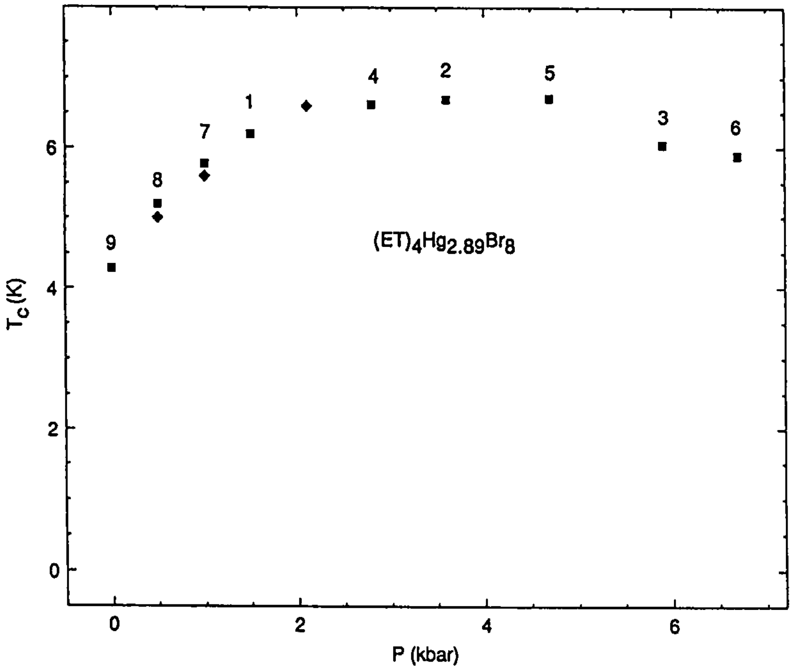

FIGURE 2 Superconducting transition temperature vs pressure for $(ET)_4Hg_{2.89}Br_8$. The numbered points are for the crystal with ~45% Meissner effect. The other points are for the crystal which had ~1% Meissner signal. The numbering denotes the order in which the points were taken.

While various correlations between unit cell volume and anion size have been suggested[27] no microscopic model for these systems has yet emerged to aid the materials synthesis in the quest for higher-T_c candidates. The obvious tack of changing anions or cations in the indicated size directions too often resulted in changing entirely the crystal structure, invariably to one which was not superconducting. The extraordinarily large pressure derivatives in the $(ET)_nX_m$ family would seem to offer the possibility of less radical changes such as alloying which might retain the favorable structural arrangement and still increase T_c appreciably. The counter argument to this approach is that alloying (unless resulting in an ordered structure) may introduce disorder which considerable evidence shows is detrimental to superconductivity in the $(ET)_2X$ family.[28]

$(ET)_4Hg_{2.89}Br_8$ and its positive pressure derivative need further study in order to understand what is happening to the structure, both electronic and crystal, so as to exploit this new behavior in synthesis of higher T_c materials.

CONCLUSION

We have summarized and discussed pressure studies of organic superconductors in general, and the $(ET)_nX_m$ family of organic superconductors in particular, where the materials were all single crystals and hydrostatic pressures were used in the same apparatus to facilitate intercomparison of all the known superconducting members. The pressure derivatives are extremely large and negative except for the newest member of the series which has a positive derivative until, presumably, a phase change into a structure in which the more conventional behavior occurs. In lieu of microscopic models, our study suggests need for an effort to understand this new non-monotonic behavior as well as alloying (both cation and anion) to exploit these large pressure derivatives.

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