Near constancy of the pressure dependence of T_c across families of organic and fullerene superconductors

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Pressure strongly depresses the superconducting transition temperature T_c of both the doped fullerenes and the β-ET[(BEDT-TTF)$_n X_m$, (BEDT-TTF)=bis(ethylenedithio)tetrathiofulvalene)] organic superconductors. An outstanding puzzle in these materials is the weak variation dT_c/dP across families of compounds with large variations in T_c. This property has been used to argue against phonon-induced pairing. However, closer examination of the volume dependence of T_c reveals that the weak variation of dT_c/dP is consistent with moderate (but not weak) electron-phonon coupling.

While the transition temperatures of the β-ET[(BEDT-TTF)$_n X_m$, (BEDT-TTF)=bis(ethylenedithio) tetrathiofulvalene)] family of organic superconductors vary over roughly an order of magnitude from $T_c \sim 1-8$ K, the pressure derivative of the transition temperature T_c remains roughly constant at $\sim 0.7-1$ K/kbar.[1,2] T_c in the alkali-doped fullerenes varies from $\sim 4-30$ K,[3–5] while dT_c/dP remains within the narrow range of $\sim 0.7-1.2$ K/kbar.[5–7] The relative insensitivity of the pressure dependence of T_c to strong variations in T_c has been taken as evidence of a non-phonon mechanism in the organic superconductors.[8,9] This conclusion results from consideration of the BCS model weak-coupling formula for T_c as a function of the Debye frequency ω_D and the electron-phonon coupling λ,

$$T_c = 1.13\omega_D e^{-1/\lambda}, \tag{1}$$

which has an exponential dependence on $1/\lambda$. Taking derivatives with respect to pressure will preserve this exponential dependence, leading to the conclusion that the pressure dependence of T_c is a sensitive function of λ. However, Eq. (1) is a notoriously bad predictor of T_c. The formula is only valid in the limit of weak coupling, on the order of $\lambda \leqslant 0.3$, values which imply very small transition temperatures. In contrast, reasonably accurate semiquantitative results for arbitrary λ can be obtained from analytic approximations of the Eliashberg equations such as the Kresin-Barbee-Cohen formula for T_c,[10,11]

$$T_c = 0.26\frac{\sqrt{\langle\omega^2\rangle}}{\sqrt{e^{2/\lambda}-1}}. \tag{2}$$

The frequency prefactor $\sqrt{\langle\omega^2\rangle}$ is measure of the characteristic phonon frequency.[11] The Kresin-Barbee-Cohen expression is reasonably accurate over the entire range from weak to strong coupling, neglecting Coulomb repulsion. The two-square-well approximation provides an alternative T_c expression which includes the Coulomb repulsion. To wit,

$$T_c = 1.13\omega_D e^{-(1+\lambda)/(\lambda-\mu^*)} \tag{3}$$

with Coulomb repulsion μ^*.

We examine volume derivatives rather than pressure derivatives, since theoretical arguments apply more directly to changes in volume. The small variations in bulk modulus across a family are in any case inconsequential on the scale of the variations in T_c. The Kresin-Barbee-Cohen expression implies

$$\frac{dT_c}{dV} = \frac{0.26}{(e^{2/\lambda}-1)^{1/2}}\frac{d\sqrt{\langle\omega^2\rangle}}{dV} + \frac{e^{2/\lambda}}{(e^{2/\lambda}-1)^{3/2}}\frac{0.26\sqrt{\langle\omega^2\rangle}}{\lambda^2}\frac{d\lambda}{dV} \tag{4}$$

with the volume dependence of T_c decomposed into terms arising from the volume dependences of $\sqrt{\langle\omega^2\rangle}$ and λ. A similar expression can be derived from the two-square-well formula, namely

$$\frac{dT_c}{dV} = 1.13e^{-(1+\lambda)/(\lambda-\mu^*)}\left[\frac{d\omega_D}{dV} + \frac{d\lambda}{dV}\omega_D\frac{1+\mu^*}{(\lambda-\mu^*)^2} - \frac{d\mu^*}{dV}\omega_D\frac{1+\lambda}{(\lambda-\mu^*)^2}\right]. \tag{5}$$

This formula has the advantage of including the Coulomb interaction and the disadvantage of reduced accuracy at large λ.

Since μ^* is reduced from the bare Coulomb interaction μ by a factor $\sim[1+\mu\ \ln(E_f/\omega_D)]^{-1}$, the increasing electronic bandwidth under compression will increase E_f and thereby decrease μ^*. The Coulomb repulsion suppresses T_c, so the contribution to dT_c/dV proportional to $d\mu^*/dV$ is negative. The logarithmic dependence of μ^* on Fermi energy implies that $d\mu^*/dV$ is small in magnitude. Since the volume derivative of the transition temperature for our materials is large and positive, we can ignore the small negative contribution from the volume dependence of μ^*.

Since phonon frequencies generally increase under application of pressure, the first term in Eqs. (4) and (5) is negative. The large positive experimental values for dT_c/dV then imply that the dominant term in the volume dependence is not the term proportional to $d\sqrt{\langle\omega^2\rangle}/dV$, but the term proportional to $d\lambda/dV$.

The electron-phonon coupling λ can be written as

$$\lambda \propto N(0)\frac{\langle x\rangle^2}{\tilde{\omega}^2}, \tag{6}$$

where $N(0)$ is the density of states at the Fermi level, $\langle x\rangle$ is a dipole matrix element of the phonon amplitude, and $\tilde{\omega}$ is an average phonon frequency. We consider the volume dependence of each of these contributions in turn.

The volume dependence of the dipole matrix elements and phonon frequencies depends on the character of the phonon modes involved. Much evidence suggests that superconductivity in the doped fullerenes is dominated by the high-frequency intramolecular phonon modes.[12–19] The evidence in the organics is more equivocal.[20] We concentrate on the case of intramolecular phonons, later generalizing to include the effects of coupling to intermolecular modes. Compression preferentially contracts the weak intermolecular bonds in both materials and only weakly affects the high-frequency intramolecular vibrations. We assume that the intramolecular phonon dipole matrix elements and intramolecular phonon frequencies are independent of volume for the pressures relevant to experiment.[21]

Since the electronic band dispersion in the organic superconductors and doped fullerenes arises from relatively weak electronic overlap between neighboring molecules, the density of states at the Fermi level decreases sharply with decreasing volume.[22] We assume a simple form for the volume dependence of the density of states, namely $N(0)=a(V-V_0)^m$ with a, V_0, and m as fitting parameters. The major results of this work are insensitive to a and V_0 and only moderately sensitive to the exponent m.

Having revealed the important volume dependencies, we next derive T_c and dT_c/dV using both the Kresin-Barbee-Cohen and two-square-well T_c formulas. The formulas are complementary in that the two-square-well results are most valid at weaker coupling and the Kresin-Barbee-Cohen results become more accurate at stronger coupling. For the two-square-well model we take the Coulomb repulsion $\mu^*=0.1$, a value typical of many superconductors (other values of μ^* do not substantively alter the conclusions). For superconductivity mediated by intramolecular phonons, the variations in T_c across a family of compounds are caused by variations in λ, not in the intramolecular phonon frequencies or Coulomb repulsion, both of which are expected to be relatively constant across a family. The results are presented as T_c and dT_c/dV as functions of λ. The pressure dependence of dT_c/dV shows an exponential-like dependence on λ at weak coupling in accord with the BCS model of Eq. (1). Similar behavior for dT_c/dV has been obtained for first-principles calculations of the superconductivity in weakly coupled aluminum.[23] At larger λ, however, the curves flatten out. The behavior is robust: the parameter a in the expression for the density of states $N(0)=a(V-V_0)^m$ enters only as an overall scale, V_0 has no effect, and the exponent m only slightly affects the character of the volume dependence. The relevant range of λ for organic and fullerene superconductors is roughly $0.5<\lambda<1.5$, a range over which T_c varies by a factor of 7 (two-square-well) or 4.5 (Kresin-Barbee-Cohen), while dT_c/dV varies by only a factor of 1.3 (two-square-well, $m=2$) or 1.2 (Kresin-Barbee-Cohen, $m=2$). In all cases, the variation in T_c is several times larger than the variation in dT_c/dV.

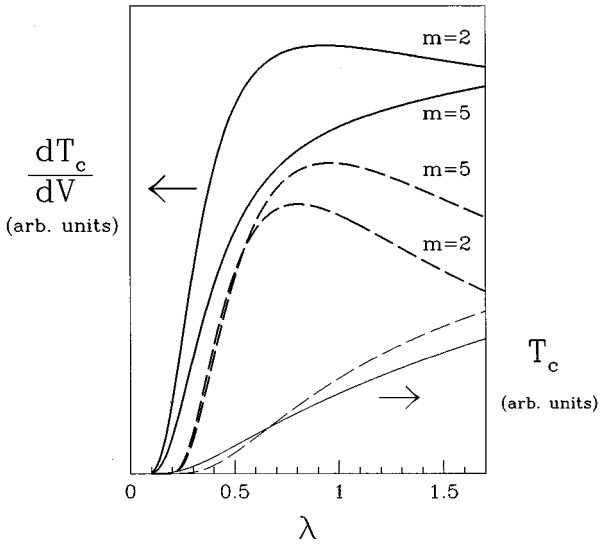

FIG. 1. The variation in T_c and dT_c/dV as a function of λ for volume-independent intramolecular phonons and a density of states of the form $N(0)=a(V-V_0)^m$. The solid curves use the Kresin-Barbee-Cohen equation. The dashed curves use the two-square-well formula with $\mu^*=0.1$. Units for T_c are arbitrary, but the same for both formulas. Units for dT_c/dV are arbitrary for each curve.

The weak λ dependence of dT_c/dV is easily explained by considering the curvature of T_c as a function of λ. If the volume dependence of λ is roughly linear, then dT_c/dV has positive slope wherever $T_c(\lambda)$ has positive curvature and negative slope wherever $T_c(\lambda)$ has negative curvature. A glance at Fig. 1 bears out this qualitative assertion. In the region where the transition temperature is nearly linear in λ, dT_c/dV is roughly constant.

Similar arguments would apply if superconductivity in the organics arose from coupling to *inter*molecular phonons with a complicated pressure dependence. In this case, volume-dependent changes in phonon frequency affect T_c in two ways: directly through the $d\omega/dV$ term of Eqs. (4) and (5) and indirectly through changes in λ via Eq. (6). Intermolecular phonon frequencies typically increase in frequency under compression. The sign of the direct term disagrees with experiment, so we concentrate on the indirect term. The exact volume dependence of the intermolecular phonons is a complex issue. However, as long as this dependence is smooth and monotonic, we may approximate λ as roughly linear in volume. So long as λ is roughly linear in volume, the volume dependence of T_c at moderate coupling is only weakly dependent on λ whatever the source of the variation in coupling. Whether λ variation arises from a volume-dependent phonon frequency or a volume-dependent density of states, dT_c/dV at moderate coupling is only weakly dependent on λ.

In summary, the small variation in dT_c/dP in the organic superconductors and the doped fullerenes can be viewed as a natural consequence of moderate electron-phonon coupling and cannot be taken as evidence of nonphononic superconductivity.

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