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Simple estimate of electron-phonon coupling in small fullerenes

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Simple scaling arguments show how contributions to the electron-phonon coupling strength vary with the number of atoms in a carbon fullerene. Smaller fullerenes have higher curvature, which yields larger electron-phonon coupling. The enhancement in coupling is inversely proportional to the number of atoms in the fullerene molecule. Recent *ab initio* theoretical results on C_{36} fit well within this simple model. [S0163-1829(99)14125-0]

The superconducting transition temperatures of threefold-coordinated carbon metals of different dimensionality vary from unmeasurably small (e.g., undoped graphite) through fractions of a Kelvin[1] to 40 K or more[2] in doped C_{60}.[3] Recently, detailed *ab initio* calculations suggest that even higher transition temperatures might be possible in doped fullerite C_{36}.[4] Since the characteristic phonon frequencies do not vary greatly between different allotropes, the variations in the superconducting T_c must arise primarily from changes in the electron-phonon coupling strength λ. Here I present a very simple model for understanding trends in the electron-phonon interaction potential for fullerenes of different sizes.

Curvature-induced hybridization in the fullerenes opens additional electron-phonon scattering channels which are not available to a flat graphitic sheet.[5] The π-derived electron-phonon interaction decomposes into two parts: a base coupling present in a flat graphitic sheet and a curvature-dependent coupling. The electron-phonon matrix elements are of the form $M_{ij}=\langle\phi_i|\delta U|\phi_j\rangle$, where ϕ_i and ϕ_j are electronic states at the Fermi level and δU is the change in the electron-ion interaction potential U upon unit distortion of a phonon mode. A phonon distortion polarized perpendicular to a flat graphitic sheet produces an interaction potential δU which is odd under reflection in the basal plane. Matrix elements of δU between electronic states with either even or odd parity vanish by symmetry (only matrix elements coupling, e.g., $\sigma\leftrightarrow\pi$ or $\sigma^*\leftrightarrow\pi^*$ states are nonzero and these states typically are well separated in energy). The curvature in a fullerene introduces an even term into δV and also admixes a small amount of opposite-parity character into the electronic states. These extra terms open up new channels for electron-phonon coupling which are absent in the flat sheet. Since these effects are first order in the curvature $1/R$, the change in λ or $|M|^2$ is proportional to $1/R^2$.

The total electron-phonon interaction potential $V_{\text{total}}\propto|M|^2$ decomposes into a piece which is present in a flat sheet and another which originates in the new scattering channels opened by finite curvature, i.e., $V_{\text{total}}=V_{\text{flat}}+V_{\text{curve}}/N$, where $N\propto R^2$ is the number of atoms in the fullerene. These two terms can be estimated using data for KC_8 doped graphite and K_3C_{60}, similar to the method of Ref. 6. The measured T_c yields an estimate of λ, which, when coupled to the measured (or calculated) density of states, yields V.

Both π^*-derived and alkali-derived states contribute to the density of states at the Fermi level in KC_8,[7] raising the question of how to extract the purely π^*-derived contribution for the present analysis. Fortunately, this question has only minor repurcussions on the final results for smaller fullerenes, as will be shown below. The Fermi surface of KC_8 contains π^*-like tubes at the edges of the Brillioun zone and two three-dimensional alkali-derived pockets at the center of the zone. The π^*-like sheets give the larger contribution to the density of states at the Fermi energy,[8] and the material's strongly anisotropic superconductivity[1,9] demonstrates that the π^*-derived states have a prominent role in the superconductivity. Two different assumptions provide reasonable upper and lower bounds on the π^*-like contribution to the electron-phonon matrix elements. To wit, either the electron-phonon coupling matrix elements are constant across the entire Fermi surface (which probably overestimates the alkali-derived contribution to V) or the π^*-derived states dominate the electron-phonon coupling in KC_8. Making a conservative error analysis [i.e., taking a Coulomb repulsion μ^* in the range $0.05\leftrightarrow0.15$ (KC_8) or $0.1\leftrightarrow0.2$ (K_3C_{60}) and an average phonon frequency of $\sim1000-1500$ K], inversion of the Eliashberg equations then yields λ for both KC_8 and K_3C_{60}. Given the Fermi-level densities of states for KC_8 (Ref. 8) and K_3C_{60},[10] we then extract V_{flat} and V_{curve}.

These parameters then allow us to estimate the π^*-derived electron-phonon interaction as a function of the number of atoms in the fullerene:

$$V_{\text{total}}\approx(1.25\pm0.7)+(130\mp40)/N \tag{1}$$

eV atom. The expression is normalized *to one atom* to ease comparison between fullerenes of different sizes.[11] (V_{total} is then multiplied by the density of states per atom per eV to obtain λ.) This simple formula yields $\lambda\approx0.3$ for doped graphite (the $N\rightarrow\infty$ limit), in accord with its low T_c of about 0.15 K.[1] For C_{60}, one obtains $V\approx57$ meV-C_{60} and $\lambda\approx1$, in good agreement with both theoretical calculations[12] and experimental results.[13]

The two errors in Eq. (1) are coupled, in that an upwards deviation in the first term implies a downwards deviation in the second. Therefore these errors partially cancel each other in predictions for the smaller fullerenes. For the recently

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synthesized[14] bulk C_{36} ($N=36$) this simple formula predicts $V\approx 135\pm 11$ meV-C_{36}, in very reasonable agreement with *ab initio* results of 130–180 meV-C_{36}.[4]

This very simple model ignores material-specific variations in electronic hybridization and the detailed effects of on-ball rotational symmetry, which can affect the number and magnitude of the nonzero matrix elements. Luckily, these symmetries have two countervailing effects: high rotational symmetry generally implies fewer nonzero matrix elements, but the remaining terms tend to be weighted more strongly due to increased electronic degeneracy in symmetric systems. In any case, such a simple model should provide only trends, not specific quantitative predictions. The present calculations also concern only the coupling matrix elements comprising V, independent of any variations in the density of states; the density of states at the Fermi energy can vary widely even for a single fullerene species [e.g., the scaling of T_c with lattice constant in A_3C_{60} (Ref. 15)] and so lies outside the scope of the present model, which simply provides an easy way to understand trends in V_{total} with the size of the fullerene molecule.

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