cally resilient diamond is preferentially formed over the thermodynamically favored graphite structure. As in the case of Si, it is likely that a more controlled exposure to hydrogen atoms will allow additional flexibility in the growth of these and other non-equilibrium materials.

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Isotope Effect in Superconducting Fullerenes

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The effect of isotopic substitution on the superconducting transition temperature, T_c, in alkali-doped C_{60} has been examined. Paradoxically, it is found that a substantial decrease in T_c with the increasing isotopic mass is possible even when the attractive interaction is not mediated by phonons but is instead of purely electronic origin. In particular, it is shown that the experimentally measured isotopic shifts are consistent with a recently proposed electronic mechanism. Further predictions are presented that can be tested by experiment.

Measurement of the isotope shift of the superconducting transition temperature, T_c, was one of the classic experiments (*1*) that established the essential role of the electron-phonon interaction in those simple metallic superconductors that are well described by the theory of Bardeen, Cooper, and Schrieffer (BCS). In this report, we wish to examine this effect in a new light—that is, in the context of a recently proposed electronic mechanism of the superconductivity of doped fullerenes (*2, 3*). We demonstrate that such a mechanism can lead to an isotope effect, and the observed magnitudes of δT_c are consistent with microscopic estimates we make in the context of the electronic mechanism (*4*). Moreover, we make further predictions of the pressure and the dopant species dependence of the isotope shift that are susceptible to experimental test.

The isotope effect is conventionally characterized by an exponent x, where $T_c \alpha M^{-x}$, where M is the mass of the isotope. Recent experiments have led to widely differing values of x, ranging from 0.3 to 1.8 in Rb-doped C_{60} (*5, 6*). (It is important to note that such a power law dependence, while natural in the context of the conventional BCS theory, is not self-evident. A better characterization is the ratio $\delta T_c/T_c$, where δT_c is the shift of the transition temperature upon isotopic substitution. For Rb_3C_{60} with $T_c \approx 30$ K, values of δT_c have been reported by different groups ranging from −0.5 to −1.5 K.) As has been already noted (*5*), it is difficult to obtain an $x > 0.5$ in the context of a conventional electron-phonon mechanism. From the discussions given in this report, it follows that no such natural upper bounds exist for the proposed electronic mechanism for the superconductivity of fullerenes.

In the proposed electronic mechanism for superconductivity in doped C_{60}, we have computed the effective attraction, E_p, between electrons at an average electron density of three extra (conduction) electrons per molecule. Once the strength of the attraction is determined, T_c can be estimated in accordance with mean-field theory,

$$T_c \propto W \exp\{-W/E_p\} \qquad (1)$$

Here W is the inverse of the density of states at the Fermi energy (which is proportional to the intermolecular bandwidth) and hence characterizes the hopping rate of the electrons between molecules. Undoubtedly, the prefactor in this equation will be modified by fluctuation effects, but we expect the exponent to be correct as long as the BCS mean-field theory of superconductivity is approximately valid. Because the isotope effect that we shall derive depends predominantly on the exponent, we can use this simple equation with impunity. Note, of course, this expression is valid only as long as E_p is positive. The important question is how does the pair-binding energy E_p depend on isotopic substitution?

For M_3C_{60}, where M is the alkali dopant, E_p is given by (*3*)

$$E_p \approx -0.05U + 0.015\frac{U^2}{t} + \ldots$$

$$= AU\left(\frac{U}{t} - x_c\right) + \quad \ldots, \qquad (2)$$

where $A = 0.015$ and $x_c = 3.4$ and U is the effective Coulomb repulsion on a carbon atom in the C_{60} molecule. The hopping matrix element t characterizes the delocalization of a π-electron on the molecule. Actually, there are two such matrix elements—one for the bonds on the pentagons t, and one for the bonds connecting the pentagons t'. It is believed (*7*) that $1.0 < t'/t < 1.3$. In the above expression we have set $t'/t = 1.2$, although similar expressions are known over the whole range of t'/t (*2, 3*). The above approximate expression is the result of second-order perturbation theory in U/t. However, if there exists a critical value of U/t denoted by x_c at which E_p becomes positive, then in the neighborhood of x_c, the dependence of E_p on U/t is linear. That an attractive effective interaction is not an artifact of second-order perturbation theory has been amply demonstrated by exact numerical calculations on smaller clusters (*8*) and, indeed, the shifts in x_c due to higher order terms are generally found to be small. The precise value of the pair-binding energy depends on the precise values of U and t, which are only known approximately. [As discussed earlier (*2, 3*), we expect U to be of order 5 to 10 eV and t to be between 2 to 3 eV.]

Clearly, for there to be an isotope dependence of T_c, E_p (equivalently t) or W must depend on the isotopic mass. In general, we expect that there will be a mass dependence of t: as a function of increasing M the zero-point fluctuations of the carbon atoms decrease; hence the mean separation between the atoms decreases, in much the same way that the lattice constant of a solid decreases with decreasing temperature. As the separation l between the carbon atoms decreases, t increases, so we expect t to be an increasing function of M. Thus, it is easy to see from Eqs. 1 and 2 that T_c decreases as M increases, provided W remains constant.

It could also be argued that the reduction of the carbon-carbon bond length on a given molecule could give rise to a decrease of the lattice constant of the solid, which,

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in turn, would increase W, hence producing a further decrease of T_c. However, because of the dominantly ionic nature of the solid, this effect is likely to be small (*5*). [For a covalently bonded solid, this could have been an important effect (*4*).] Therefore, even though a sizable change of the lattice constant of the solid is not expected, the increase in t and the consequent decrease in E_p are sufficient to give rise to an isotope effect of the same magnitude as that seen in recent experiments. The detailed calculation of δt follows. In the present section we shall summarize the important formulae.

From a knowledge of U, t, δt, and W one can easily calculate δT_c. However, this involves a large number of parameters. We can reduce this number by noting that because δt is expected to be small, to linear order in δt we may write

$$\frac{\delta T_c}{T_c} = -A\left(\frac{U}{t}\right)^2\left(\frac{\delta t}{W}\right)\ln^2(W/T_c) \tag{3}$$

On the other hand, because E_p is small compared to W for the observed values of T_c, it is sufficient to replace (U/t) by x_c in Eq. 3. This avoids having to explicitly specify U and t; all we need is the critical value of (U/t) at which the pair-binding energy E_p becomes positive.

It is worth noting that the ratio $(\delta T_c/T_c)$ for different dopant species can be expressed in a form that only depends on the observable quantities. Thus,

$$\frac{(\delta T_c/T_c)_{\mathrm{Rb}}}{(\delta T_c/T_c)_{\mathrm{K}}} = \frac{[(1/W)\ln^2(W/T_c)]_{\mathrm{Rb}}}{[(1/W)\ln^2(W/T_c)]_{\mathrm{K}}} \tag{4}$$

Similarly, the pressure dependence of $(\delta T_c/T_c)$ is contained in Eq. 3; U, t, A, and δt, being primarily the properties of a single molecule, are expected not to change with pressure. The dependence on pressure is entirely characterized by W and T_c, which are measurable (*9*).

The hopping matrix element t between two atoms as a function of the change of the carbon-carbon bond length δl is

$$t = t_0 - \alpha\delta l + \frac{1}{2}\beta\delta l^2 + \ldots \tag{5}$$

As the lattice executes its zero-point motion, the value of δl fluctuates, leading to a small modulation of t. Because the intramolecular phonon frequencies are slow compared to the intramolecular electronic energies, we can use the adiabatic approximation. This means that the electronic spectrum should be calculated for each possible distorted configuration of the C_{60} molecule, and the result averaged over the lattice ground-state wavefunction. Because this effect is small, we can compute the expectation value of E_p according to

$$\langle E_p\rangle = E_p(\{\langle t_{ij}\rangle\}) + \frac{1}{2}\sum_{\langle ij\rangle\langle kl\rangle} d^2E_p/dt_{ij}dt_{kl}[\langle t_{ij}t_{kl}\rangle - \langle t_{ij}\rangle\langle t_{kl}\rangle] + \ldots \tag{6}$$

where $\langle ij\rangle$ signifies nearest-neighbor sites and t_{ij} is the configuration-dependent hopping matrix element between the sites i and j. To calculate the first term, it is only necessary to calculate the change in E_p under a uniform change of t, and separately to compute the isotope-dependent shift in t. The higher order terms involve recomputing E_p in the presence of all possible (weak) static lattice distortions. Although this is a rather involved calculation, the higher order terms can easily be shown to make a smaller contribution. We therefore neglect the higher order terms.

Thus, in the presence of quantum fluctuations of the carbon atoms,

$$\delta t \approx -\alpha\langle[(\mathbf{u}_i - \mathbf{u}_j)\cdot\hat{\mathbf{e}}_{ij}]\rangle - \frac{\alpha}{2l}\{\langle[(\mathbf{u}_i - \mathbf{u}_j)\times\hat{\mathbf{e}}_{ij}]^2\rangle - \frac{\beta l}{\alpha}\langle[(\mathbf{u}_i - \mathbf{u}_j)\cdot\hat{\mathbf{e}}_{ij}]^2\rangle\} \tag{7}$$

where i and j are a pair of nearest-neighbor sites, $\mathbf{u}_j$ is the displacement of the atom at site j from its classical equilibrium position, and $\hat{\mathbf{e}}_{ij}$ is a unit vector pointing from the site i to the site j. The linear term in Eq. 7 is zero in the harmonic approximation, but is non-zero when anharmonic effects are taken into account. All three terms that contribute to δt are easily seen to be proportional to ϖ, an appropriate average of the phonon frequency (defined below), hence proportional to $M^{-1/2}$, while all the neglected higher order terms are higher order in $M^{-1/2}$. To lowest order in $M^{-1/2}$, the linear term can be computed to lowest order in the cubic anharmonicity and the quadratic terms can be computed to zeroth order (harmonic approximation).

To compute the linear term, which represents an M-dependent lattice expansion, one needs to know the cubic anharmonicity. This is difficult to obtain from model calculations, but can be estimated from the thermal expansion, because it involves same anharmonic terms. In particular, at high enough temperatures such that the lattice of atoms can be treated classically, but low enough that the anharmonic terms can be treated perturbatively, one finds (*10*)

$$\langle u\rangle_T = \kappa_\infty T \tag{8}$$

where $\langle\rangle_T$ represents the thermal expectation value. (We adopt units in which $\hbar = k_B = 1$.) It is easy to see that

$$\langle u\rangle_{T=0} = \frac{1}{2}\kappa_\infty\varpi \tag{9}$$

where the appropriate average over the phonon frequencies, ϖ, is given straightforwardly in terms of matrix elements of the anharmonic terms in the potential. To estimate an appropriate average of the phonon frequencies, we have computed the average phonon frequency ϖ_1 and the inverse of the average inverse phonon frequency ϖ_2 weighted by the mean-square change in the bond length. The model of the electron-phonon coupling used is discussed in detail elsewhere (*11*). In this model we include bond-stretching and bond-angle couplings in addition to the purely electronic Hubbard Hamiltonian (*2*, *3*). With this Hamiltonian we have obtained an excellent description of the phonon spectrum, as well as of the infrared absorption of C_{60} (*11*). We find that $\varpi_1 = 0.17$ eV and $\varpi_2 = 0.16$ eV. That these two averages do not differ greatly from each other illustrates the insensitivity of the results to the precise definition of the average. Because the thermal expansion of an isolated C_{60} molecule at temperatures higher than the largest intramolecular phonon energy (≈ 0.2 eV) is not known, we obtain κ_∞ from the known in-plane thermal expansion coefficient of graphite (*12*) extrapolated to temperatures larger than the Debye temperature; κ_∞, thus determined, is 2.6×10^{-2} Å eV^{-1} (*13*). As a result, we find that the change due to the isotopic substitution is

$$\delta\langle[\mathbf{u}_i - \mathbf{u}_j)\cdot\hat{\mathbf{e}}_{ij}]\rangle = 2\times10^{-3}[1-({}^{12}M/M)^{1/2}]\ \text{Å} \tag{10}$$

where ${}^{12}M$ is the mass of ${}^{12}C$.

In order to evaluate Eq. 6, we consider the same model of the electron-phonon coupling in C_{60} mentioned earlier (*11*). We find, again, for the changes due to the isotopic substitution:

$$\delta\langle[\mathbf{u}_i - \mathbf{u}_j)\times\hat{\mathbf{e}}_{ij}]^2/2l\rangle = 2\times10^{-3}[1-({}^{12}M/M)^{1/2}]\ \text{Å} \tag{11}$$

$$\delta\langle[\mathbf{u}_i - \mathbf{u}_j)\cdot\hat{\mathbf{e}}_{ij}]^2/2l\rangle = 7\times10^{-4}[1-({}^{12}M/M)^{1/2}]\ \text{Å} \tag{12}$$

Finally, these results can be combined to obtain an expression for δt attributable to the isotopic substitution, with the previously discussed (*11*) values of the parameters, $t_0 \approx 2.5$ eV and $\alpha \approx 5$ eV Å^{-1}. We have used various methods (*14*) to obtain an empirical estimate of the parameter $\beta l/\alpha$ and have obtained results between 0 and 3. Because our primary interest here is in the rough magnitude of the effect, we will adopt the value $\beta/l\alpha = 0$ so as not to introduce an additional parameter. As a result, we find

$$\delta t \sim 20[1-\sqrt{{}^{12}M/M}]\ \text{meV} = 0.8\ \text{meV} \tag{13}$$

where the final equality is for 100% substitution with ${}^{13}C$. Larger values of $\beta l/\alpha$ will result in slightly lower estimates for δt. Various experimental probes of W in Rb_3C_{60} with $T_c \approx 30$ K yield estimates in the range 0.1 to 0.5 eV (*15*). For these parameters, we find $|\delta T_c|$ in the range 0.6 to 0.2 K. We reiterate that the absolute magnitude of δt, and hence of δT_c, is difficult to compute to better than a factor of 2 accuracy; the trends, however, as a function of W and T_c implied by Eq. 3 should be reliable and testable experimentally.

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Presence of the Earliest Vertebrate Hard Tissues in Conodonts

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From histological investigations into the microstructure of conodont elements, a number of tissue types characteristic of the phosphatic skeleton of vertebrates have been identified. These include cellular bone, two forms of hypermineralized enamel homologs, and globular calcified cartilage. The presence of cellular bone in conodont elements provides unequivocal evidence for their vertebrate affinities. Furthermore, the identification of vertebrate hard tissues in the oral elements of conodonts extends the earliest occurrence of vertebrate hard tissues back by around 40 million years, from the Middle Ordovician (475 million years ago) to the Late Cambrian (515 million years ago).

Since their first description (*1*), debate over the phylogenetic affinities of conodonts has persisted, encompassing such diverse groups as algae, vascular plants, numerous invertebrate phyla, chordates, and vertebrates (*2*). The recent discovery and interpretation of conodonts with preserved soft tissue (*3, 4*) has led to increased support for chordate affinity (*4, 5*), although alternative hypotheses based on the soft-bodied specimens have postulated a relation with aplacophoran mollusks (*6*) or chaetognaths (*7*). The group has also been considered to possess sufficient novel characters to warrant phylum status (*8*).

The only hard parts of these animals, the conodont elements, are composed of carbonate fluorapatite (*9*) with a matrix of collagen and other organic material (*10*). Elements are located in the oral cavity and are thought to have had a food-processing function analogous with teeth (*11*). They are internally divisible into a basal body, lamellar crown, and white matter (*12*) (Figs. 1A, 2A, and 3, A and D). Given the chemical and morphological similarity of the elements to vertebrate tissues, it has been variously proposed that the lamellar crown is homologous with enamel (*13*), enameloid (*5, 14*), acellular bone (aspidin) (*15*), or the unmineralized keratinous teeth of myxinoids (*16*), whereas the basal tissue has been compared with dentine (*5, 13, 14*), bone (*18*), and cartilage (*18*). Previous studies have not, however, clearly demonstrated histological homology between conodont elements and vertebrate teeth (*19*), and it has generally been concluded that the elements are composed of tissue types confined to conodonts. White matter, in particular, has been regarded as a novel and enigmatic tissue, arising from secondary modification of the lamellar crown (*20*), although Krejsa *et al.* (*16*) proposed homology between white matter microspaces and tubules in *Ozarkodina confluens* (Branson and Mehl) and structures associated with pokal cells and parakeratotic keratin in the lingual elements of myxinoids.

The conodont elements we have prepared (*21*) were compared with similar preparations of vertebrate skeletal material from the Harding Sandstone, Canon City, Colorado, the earliest unequivocal vertebrate hard tissues that are histologically intact (*22, 23*). Three genera are present in the Harding material (*14, 19*), each with a distinct histological association. Sclerites of *Astraspis* Walcott and *Eriptychius* Walcott are both composed of basal acellular bone (aspidin) and superficial tubercles of acellular dentine, capped by enameloid and enamel, respectively. A third, unnamed, genus has discrete tubercles composed of cellular bone and cellular dentine, and may represent a stem group osteostracan (*22*).

White matter is consistently developed in all of the conodont specimens examined to date. It is characterized by lacunate spaces, interconnected by irregular, radiating tubules (Figs. 1D, 2C, and 3, B

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