

network carrying an incompressible fluid in which the inelastic strings or Zener diodes are replaced by constant-pressure-difference valves (sometimes called pressure-relief valves or safety valves) and the elastic springs or linear resistors are represented by tubing of appropriate length with incompressible viscous (Poiseuille) flow; fluid flow is then analogous to weight or electrical current, and pressure difference is analogous to extension or voltage drop⁷. In an analogous thermal network, heat flow corresponds to weight or current, and temperature difference corresponds to extension or voltage drop⁸.

These physical paradoxes are closely connected to a paradox in traffic flow discovered by Braess¹. In an idealized traffic network, each individual seeks a minimal-cost (or shortest) path from a point of entry to a point of exit. In an uncongested network, the choices of paths through the network made by different individuals do not affect one another. Adding uncongested routes to an uncongested network can only lower, or at worst not change, the time individuals require to travel through the network from a source to a destination. A congested network differs from an uncongested one in that, for at least one arc of a congested network, the cost (per person or vehicle) of travel along that arc strictly increases with increasing traffic flow. Braess^{1,2} discovered a congested transportation network such that, if a link is added and all individuals seek their best possible route, at the new equilibrium the cost of travel for all individuals is higher than before.

Braess's paradox (additional capacity leading to more costly travel for all) occurs both in general transportation networks^{9,10} and in a queuing network¹¹. Thus Braess's paradox is not a peculiarity of the mathematical formalism Braess used to describe a transportation network, but appears to be a more general property of some congested flows. Transportation and queuing networks are special examples of non-cooperative games, for which a general analogue of Braess's paradox holds¹²: in the language of game theory, Nash equilibria of non-cooperative games are generically Pareto-inefficient.

Braess's original model translates to a mechanical network similar to Fig. 1, with each inelastic string replaced by an inelastic spring in series with a spring; or, analogously, to an electrical circuit similar to Fig. 3, with each Zener diode replaced by a Zener diode in series with a resistor. The translations among transportation networks, mechanical networks, electric circuits and hydraulic networks are exact because there is conservation at every node (traffic in equals traffic out, mechanical force upward equals mechanical force downward at equilibrium, and so on) and because different paths from one node to another, if used, must have equal cost (travel time, stretch, voltage drop or pressure drop). Analogues of Braess's paradox should also exist in continuous representations of systems that obey Kirchhoff's laws.

These mechanical and electrical analogues of Braess's paradox illustrate the possibility of counter-intuitive equilibrium

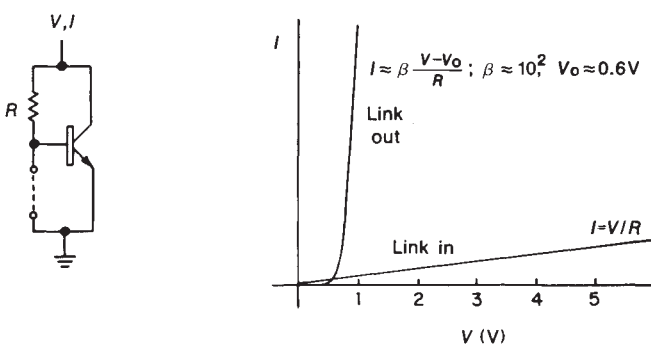


FIG. 4 A less surprising two-terminal electrical network in which an added current path (dotted) causes less current to flow from source to ground. The transistor acts as a switch.

behavior in physical networks when the load imposed on an arc affects that arc's behaviour (stretch or voltage drop, in these examples). The task remains of specifying the general conditions under which such paradoxes can occur, for general network topologies and broad classes of components, possibly including nonlinear ones. The examples presented here suggest caution in assuming that physical networks will behave as normally expected when paths or components are added. □

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Preparation and structure of the alkali-metal fulleride A_xC_{60}

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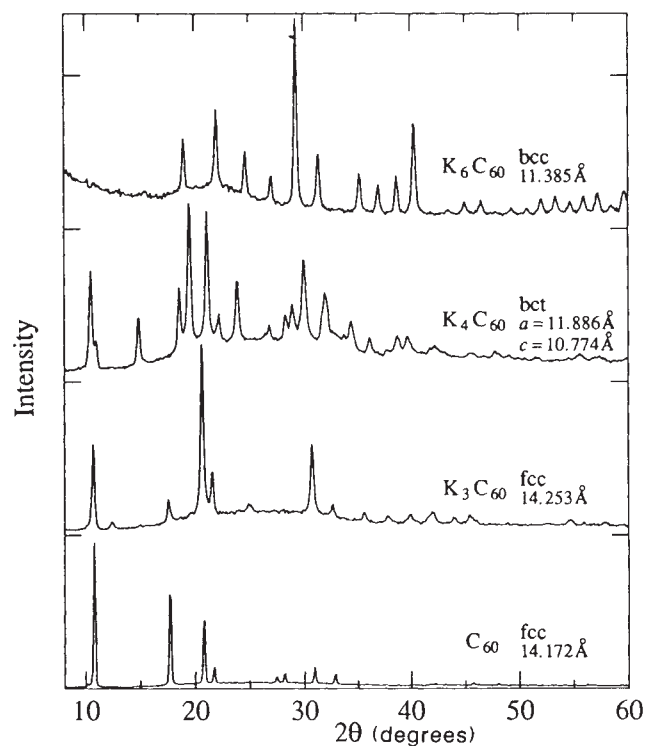
SUPERCONDUCTING K_3C_{60} (ref. 1) has been shown² to have an intercalated face-centred cubic (f.c.c.) structure, and other A_3C_{60} compounds (where A is K, Rb or mixtures of K, Rb and/or Cs) form an isostructural series with superconducting transition temperatures up to 31.3 K (ref. 3). Recently we reported⁴ ^{13}C NMR studies of K_xC_{60} for $x < 3$, and concluded that the system contained two phases ($x = 0$ and $x = 3$) for $0 < x < 3$. Here we report an investigation of A_xC_{60} in the range $3 < x < 6$ and find evidence for an additional phase at $x = 4$. In contrast to f.c.c. A_3C_{60} (refs 2, 3) and body-centred cubic A_6C_{60} (ref. 5), A_4C_{60} (where A is K, Rb, Cs) has a body-centred tetragonal structure. We show that all of the experimentally observed phases of A_xC_{60} can be predicted solely on the basis of electrostatic considerations. We have found no evidence for superconductivity in A_4C_{60} .

Rb_4C_{60} was prepared by reaction of stoichiometric quantities at 225 °C for three days followed by 400 °C for one week in sealed, evacuated Pyrex tubes. K_4C_{60} was prepared by thermal de-intercalation of K_6C_{60} by heating in an evacuated Pyrex ampoule for one week in a thermal gradient with the K_6C_{60} at 550 °C and the cold end at room temperature. After de-intercalation, X-ray diffraction showed the material to be single-phase body-centred tetragonal (b.c.t.). For Cs_xC_{60} , the b.c.t. phase has been seen thus far only in two-phase samples prepared by reaction of material with nominal composition Cs_3C_{60} .

Representative $Cu K\alpha$ X-ray powder patterns of K_xC_{60} in sealed glass capillaries are shown in Fig. 1 for $x = 0, 3, 4$ and 6. C_{60} and K_3C_{60} can be indexed as f.c.c. with the lattice parameters shown^{2,6}, whereas K_6C_{60} is body-centred cubic (b.c.c.)⁵. A_4C_{60} is neither b.c.c. nor f.c.c., but instead can be indexed with a b.c.t. unit cell with lattice parameters of $a = 11.886(7)$ and $c = 10.774(6)$ for K_4C_{60} , and $a = 11.962(2)$ and $c = 11.022(2)$ for

TABLE 1 Observed and calculated parameters for A_4C_{60} (tetragonal $I4/mmm$)

			Rb_4C_{60}			K_4C_{60}		
<i>h</i>	<i>k</i>	<i>l</i>	$2\theta_{obs}$	l_{obs}	l_{calc}	$2\theta_{obs}$	l_{obs}	l_{calc}
1	1	0	10.437	160	193	10.502	592	629
1	0	1	10.873	26	13	10.982	169	109
2	0	0	14.785	125	153	14.884	278	343
0	0	2	16.079	149	126	16.43*	0	1
1	2	1	18.42*	0	1	18.627	394	490
1	1	2	19.216	654	767	19.526	1,000	1,000
2	2	0	20.997	1,000	1,000	21.142	827	784
2	0	2	21.865	109	93	22.175	124	155
1	3	0	23.50*	0	0	23.67*	0	8
3	0	1	23.718	631	693	23.926	394	386
1	0	3	25.357	66	91	25.89*	0	13
2	2	2	26.574	310	342	26.844	64	72
2	3	1	28.125	132	202	28.326	144	260
3	1	2	28.688	204	227	28.937	160	298
2	1	3	29.483	592	710	30.024	623	854
4	0	0	29.868	252	302	30.07	189	133
3	3	0	31.730	116	153	31.798	263	80
4	1	1	31.90*	0	5	32.095	0	92
0	0	4	32.482	104	48	33.26*	0	0
3	0	3	33.168	104	61	33.786	183	226
4	2	0	33.50*	0	12	33.718	40	21
4	0	2	34.107	264	355	34.451	0	10
1	1	4	34.22*	0	2	34.94*	0	75
3	3	2	35.777	155	131	36.157	101	89
4	3	1	38.488	237	166	38.799	187	89
5	0	1						
2	2	4	39.023	212	177	39.776	176	98

* Calculated 2θ .FIG. 1 X-ray powder patterns of K_xC_{60} for $x=0, 3, 4$ and 6 .

Rb_4C_{60} . Although we did not prepare Cs_4C_{60} directly, a two-phase sample of nominal composition Cs_3C_{60} contained a b.c.t. cell with lattice parameters of $a = 12.057(18)$ and $c = 11.443(18)$. For $A = K$ and Rb , the b.c.t. phase is seen in equilibrium with f.c.c. for samples with nominal compositions of A_xC_{60} with $3 < x < 4$, but is seen together with a b.c.c. second phase for samples with $4 < x < 6$. This indicates that the $x = 4$ composition is a line phase with little variation in the stoichiometry, as are $x = 0, 3$ and 6 .

The powder patterns of A_4C_{60} (where A is K, Rb, Cs) can be indexed as b.c.t., suggesting a possible space group of $I4/mmm$. We note that if the C_{60} molecules are ordered, the symmetry

can be no higher than orthorhombic (for example, $Immm$) with an accidental degeneracy of a and b . This follows from the lack of a fourfold axis in the C_{60} molecule, which prohibits it from occupying the origin of a b.c.t. cell. For A_4C_{60} to be b.c.t., the C_{60} must be orientationally disordered or rotating rapidly. We have therefore modelled A_4C_{60} for $A = K, Rb$ using $I4/mmm$ with uniform shells of electron density at $(0, 0, 0)$ and alkali-metal atoms at $(0, \frac{1}{2}, z)$. A refinement of z gives a best fit at $z = 0.28$, roughly the same fractional coordinate found⁵ for the alkali-metal positions in A_6C_{60} . The radius of the C_{60} sphere was set to 3.55 \AA , a value previously determined^{2,6} and varied manually. Changes in the sphere radius by $\pm 0.05 \text{ \AA}$ degraded

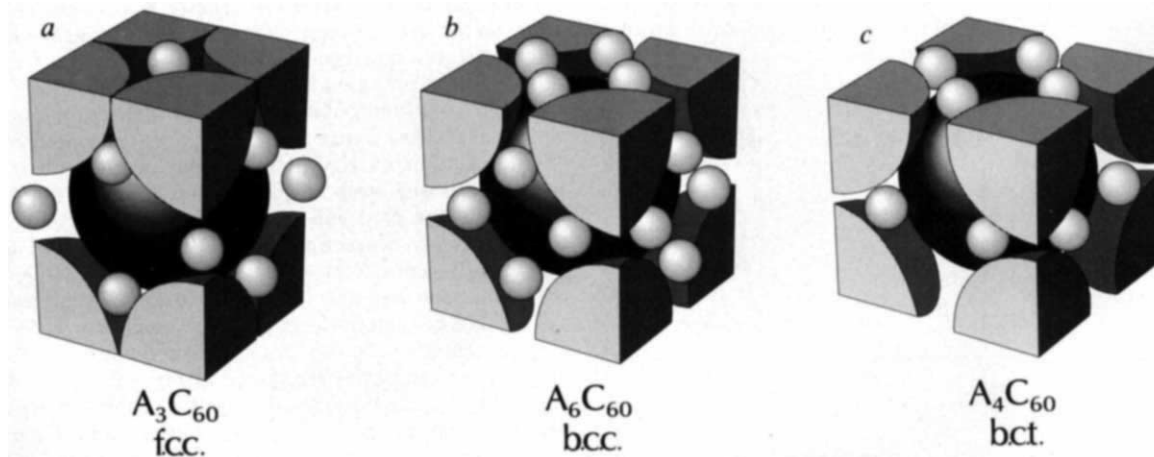
FIG. 2 Structures of A_3C_{60} , A_4C_{60} and A_6C_{60} (schematic). The f.c.c. cell has been rotated by 45° and depicted as an equivalent b.c.t. cell with $a_{bct} = a_{fcc}/\sqrt{2}$.

TABLE 2 Electrostatic calculations for Rb_xC_{60}

x	Phase	Site symmetry	Lattice (Å)	C_{60} - C_{60} (Å)	Madelung energy (eV)	Energy of $\text{C}_{60}^{\times-}$ (eV)	Total (eV)
1	f.c.c.	O	14.436	10.208	-3.49	-2.60	-6.09
2	f.c.c.	T	14.436	10.208	-5.80	-1.57	-7.37
3*	f.c.c.	O and T	14.436	10.208	-7.36	-0.23	-7.59
3	b.c.c.	O	11.787	10.208	-7.23	-0.23	-7.46
3	A15†	T	11.787	10.208	-7.16	-0.23	-7.39
4	b.c.c.	T	11.657	10.095	-8.52	1.18	-7.34
4‡	b.c.t.	T‡	11.962 (a) 11.022 (c)	10.095	-8.70	1.18	-7.52
6‡	b.c.c.	T	11.548	10.001	-11.74	4.24	-7.50

* Experimentally observed.

† Cubic $Pm\bar{3}n$.

‡ Distorted site.

the quality of the fit. Table 1 summarizes the observed and calculated intensities for K_4C_{60} and Rb_4C_{60} using these parameters.

Figure 2 shows the close relationship between the f.c.c., b.c.c. and b.c.t. sphere packing and the sites occupied by alkali metals in A_xC_{60} ($x=3, 4, 6$). The conventional f.c.c. cell has been redrawn as an elongated b.c.t. cell ($c/a = \sqrt{2}$). The f.c.c. structure has one octahedral and two tetrahedral sites per C_{60} available for alkali-metal cations. In the b.c.c. structure, there are six tetrahedral sites per C_{60} , which are 31% larger than the f.c.c. tetrahedral sites. The sphere packing in the b.c.t. structure is similar to that of b.c.c., with a compression relative to b.c.c. of $c/a = 0.906, 0.921$ and 0.949 when A is K, Rb and Cs respectively. The tetrahedral sites in the b.c.t. structure are distorted from the ideal tetrahedra in b.c.c. A_6C_{60} by $\sim 2\%$. We are now conducting measurements of the physical properties of A_4C_{60} . From d.c. magnetization measurements we find no evidence of superconductivity in any A_4C_{60} sample other than that arising from an A_3C_{60} impurity.

To provide insight into the relative stabilities of the various A_xC_{60} phases, we have calculated the electrostatic energies. Table 2 summarizes the results for Rb_xC_{60} . The Madelung contribution in electron volts per excess electron was calculated with a standard computer program assuming point charges for the Rb^+ and $\text{C}_{60}^{\times-}$ ions, with experimental lattice parameters for existing phases. The electrostatic energy of putting x electrons on a C_{60} molecule was assumed to be of the form

$$E_x = -E_A + C_x/R$$

where E_A is the electron affinity of neutral C_{60} , taken to be 2.6 eV. (A change in the assumed value of E_A would alter the absolute numbers in the last column, but the energy differences would be unchanged.) The term C_x/R is the minimum coulomb repulsion of x point charges on a sphere of radius R , with R taken to be the C_{60} radius of 3.5 Å. The total calculated electrostatic energy is expressed as the energy per excess electron per C_{60} , allowing the electrostatic contributions to be directly compared. Note, first, that the three phases with lowest calculated electrostatic energy are the three experimentally observed phases. Because of the approximate method used to estimate E_x , and the neglect of van der Waals, chemical or packing interactions, the electrostatic energies of these three phases are essentially equal. The energies of these phases are, however, significantly different from the energies of the alternatives. For $x = 4$, the electrostatic forces promote the distortion of the b.c.c. structure into the observed b.c.t. structure. Electrostatic forces alone, however, would result in a far larger effect. The relatively small observed difference between a and c must result from packing limitations. □

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Off-axis orientation of the electronic transition moment for a linear conjugated polyene

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IN many applications of conjugated polyenes for nonlinear optoelectronics and as probes of biophysical systems, the orientation of the electronic transition dipole moment relative to the long axis of the chains is an important quantity. Simple models predict that the transition moment lies closely along the chain axis^{1,2} or at an angle of about 30° to this axis³, but the difficulty of preparing perfectly oriented samples has made these predictions hard to test. Here we report the results of polarized single crystal spectroscopy of a linear conjugated tetraene in the highly aligned configuration made possible by incorporating these molecules as guests in the channels of urea crystals. The angular dependence of the absorption spectrum indicates that the transition moment lies at an angle of 15° to the chain axis. Molecular-orbital calculations can reproduce this value when they include the effects of electron correlation.

It has been stated, perhaps prematurely, that if there is anything that we understand in molecular spectroscopy, it is the electronic excitations of linear conjugated polyenes⁴. These simple conjugated chains form one of the main classes of coloured compounds such as the carotenoids. The electronic transition that gives these compounds their colour is strongly allowed, and there have been many studies of its energy, strength and vibronic structure^{1-3,5-12} since the theory of the relationship between constitution and colour was first developed. There is a renewed interest in the spectroscopy of this class of compounds because of their nonlinear optical properties and because they serve as finite models for conductive polymers¹³⁻¹⁵.

One aspect of the transition that has not received much attention is the orientation of the transition dipole relative to the direction of the conjugated chain^{9,10,16,17}. Simpson³ and Parkhurst and Anex^{16,17} recognized that this transition dipole

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