Reports

Pressure Dependence of Superconductivity in Single-Phase K_3C_{60}

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The superconducting compound K_3C_{60} (with transition temperature T_c = 19.3 kelvin at ambient pressure), formed as a single phase by reaction of alkali vapor with solids of the icosahedral C_{60} molecule (buckminsterfullerene), shows a very large decrease of T_c with increasing pressure. Susceptibility measurements on sintered pellets showing bulk superconductivity are reported up to 21 kilobars of pressure, where T_c is already less than 8 kelvin. The results are consistent with a piling up of the density of states at the Fermi level.

THE DISCOVERY OF CONDUCTING (*1*) and superconducting (*2*) alkali compounds of the icosahedral C_{60} molecule (*3*), also called buckminsterfullerene (*4*), has attracted tremendous experimental and theoretical interest (*5–13*). As the initial report was based on samples prepared from gas-solid reactions, no claim could be made about the homogeneity of the superconducting phase nor its composition or structure (*2*). It was then shown that the K:C_{60} system has only a single stable superconducting phase, K_3C_{60}, with a transition temperature T_c = 19.3 K, and samples were prepared in which this phase constitutes the majority of the material (*5*). Further refinement, described below, has allowed us to prepare samples that are bulk superconducting phase, to separate the morphology-dependent characteristics, and to resolve the structure of this stoichiometric compound (*6*). Magnetization measurements on a nearly optimized powder sample indicate K_3C_{60} to be an extreme type-II superconductor with a London penetration depth λ = 2400 Å and a coherence length ζ = 26 Å (*7*). In this respect, both K_3C_{60} and the T_c = 30 K superconductor (*5, 8*) Rb_xC_{60} are analogous to high-T_c cuprates, with a Ginzburg-Landau parameter $\kappa = \lambda/\zeta$ near 100 and comparable T_c. During the short history of these materials, there has been considerable speculation (*11–13*) about the nature of the superconductivity, with predictions of either a strong increase or strong decrease in T_c under pressure. Here we show that K_3C_{60} has a very strong negative pressure dependence of T_c. Indeed, by any measure, it appears to be among the largest reported.

The methods of powder sample preparation have been thoroughly described (*5*). Briefly, the reaction between C_{60} solid and stoichiometric amounts of K vapor proceeds in several stages, until a material that is very rich in the superconducting phase is achieved, as determined by monitoring the shielding diamagnetism. Because of limited air stability, all operations are carried out under inert gas (He) or in sealed tubes or on well-wrapped samples. Once the diamagnetic shielding reaches a terminal value above 50% by volume, the samples are subjected to one or two pressing-sintering-grinding cycles. Specifically, powder samples, prepared by reaction of 30 mg of well-dried C_{60} samples with 5 mg of K, are pressed into compact pellets at pressures of 40 bar (4×10^6 Nm^{-2}). They are then sliced into thin strips for susceptibility measurements, sintered at 200° to 250°C, remeasured, ground into fine powder, pressed again, and so on. As before (*5*), our main diagnostic of sample characteristics is the temperature-dependence of the magnetic susceptibility, $\chi(T)$, measured with a mutual inductance coil bridge, operated at 100 kHz with phase-sensitive detection and over the range 4 to 50 K. The diamagnetic fraction, defined as $\chi_{dia} = \chi_{normal} - \chi(4.2\ K)$, is expressed as a percentage of an Nb standard. The pressure measurements were performed on a solid bar of K_3C_{60}, prepared as described above by sintering the superconducting powder. The pressure dependence of T_c was determined inductively at a frequency of 457 Hz in a Be-Cu pressure cell whose design and operation have been described previously (*14*). A hydrostatic pressure environment was produced using Fluorinert FC-75 as the pressure medium, which was determined by independent experiments not to react with K_3C_{60}. The pressure within the cell was measured by the shift in T_c of a piece of high purity Pb.

Figure 1 shows four diamagnetic shielding curves for one representative sample at different stages of the pressing-sintering treatment. Curve A is the $\chi(T)$ curve of the as-prepared powder compound, K_3C_{60}, exhibiting a 60% fraction of Nb standard; this is a high figure for a powder sample that has a density in the range of one-half bulk. From this curve, one can clearly identify the onset of diamagnetic shielding at T_c = 19.3 K, which has an initially steep then gradually flattening shape as one goes to lower temperatures. This shape is characteristic of the powder, which has a grain size (near 1 μm) not much larger than the London penetration depth (λ = 0.24 μm) (*7*).

This sample was then pressed at 40 bar to obtain a nice pellet with dimensions 3 mm diameter by 0.7 mm thickness. Curve B in Fig. 1 was measured on a rectangular slice cut from the pellet ($3 \times 0.7 \times 0.7$ mm^3), with the field parallel to the long axis. Two changes are noteworthy: (i) To within our precision, a 100% shielding diamagnetism has been reached, that is, the field is completely shielded from the bulk sample at low temperatures (<10 K), the material now behaves as a perfect diamagnet. (ii) Besides the onset at T_c = 19.3 K, the shape of $\chi(T)$ in the 10 to 20 K range is quite different. Now the initial decline in χ is gradual to near 15 K, corresponding to 20% of the sample, followed by a very sharp decline starting at the latter temperature. (To distinguish the two transition temperatures, we

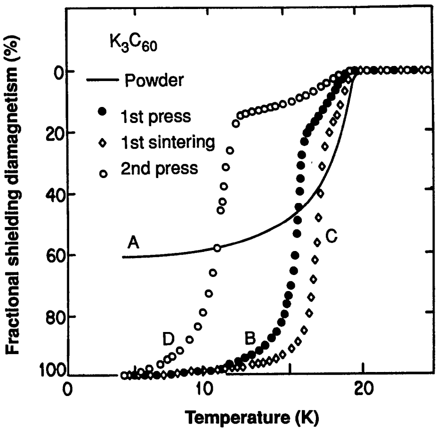

Fig. 1. Magnetic susceptibility curves $\chi(T)$ for a sample of K_3C_{60} powder, exhibiting shielding diamagnetism expressed as a percentage of an Nb standard measured at 4.2 K. Curves A, B, C, and D are for the same sample as a powder, after initially pressing, after sintering, and after a grinding and secondary pressing, respectively.

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define the higher as $T_{c1} = T_c = 19.3$ K, and the lower kink as T_{c2}.) When the same pressed sample is heated at 200°C for 12 hours and then remeasured, curve C is obtained. This curve is similar to curve B, except that the kink at $T_{c2} = 15$ K has shifted toward T_{c1}, to about 17.5 K, and the temperature range over which χ is 100% has widened. Grinding to a fine powder, and pressing again, yields curve D, in which the kink has moved down to near 10 K, that is, the higher temperature, 20% decline portion of the curve is now very gradual up to the kink at $T_c = 19.3$ K that is always present. Upon sintering again, we practically recover the shape of curve C, after the first sintering. Furthermore, the higher temperature transition T_c is not affected by a factor of 50 change in the primary excitation field or by two orders of magnitude change in the excitation frequency. However, the lower transition T_{c2} is moved to lower temperatures, by about 0.8 K, for the highest field excitation and to higher temperatures with increasing excitation frequency. These results suggest that the lower transition may arise from Josephson coupling of the superconducting K_6C_{60} particles, an effect only appearing in the sintered bars.

This kind of treatment-dependent behavior in the diamagnetism is very similar to that obtained on other sintered-powder materials, including the high-T_c cuprates. It should be interpreted in terms of weak links between the superconducting grains, prohibiting the flow of shielding current in a temperature range below T_c. The powder sample, curve A, reflects the T dependence of the individual grains, which are electrically isolated from each other, so that negligible shielding current passes among them. There is a single T_c at 19.3 K. In the pressed samples, weak electrical contacts are formed at grain-contact points. But the nature of these contacts is wholly dependent on the history of sample treatment, grain size, pressing force, and so forth. In such a pressed pellet, it is only at lower temperature that coherence among the grains is established so that a macroscopic supercurrent can flow and the field is expelled from the bulk of the sample. This occurs at a distinct temperature characteristic of the weak links between grains that is dependent on sintering, grain size, and magnetic field. Thus the second critical-like temperature, T_{c2}, is of an extrinsic nature and would not appear in a macroscopic single crystal.

To repeat, the only morphology-independent T_c in all this work and earlier, on numerous samples prepared and measured repeatedly over a 6-week period, is that at 19.3 K. All these qualitative observations indicate that K_3C_{60} is highly crystalline—in fact it is face-centered cubic (fcc) (*6*) with a structure as well defined as the insulating C_{60}-fullerite (fcc) (*15, 16*) or K_6C_{60} body-centered cubic (bcc) (*9*).

Figure 2 shows $\chi(T)$ curves for K_3C_{60} at a series of pressures from ambient to 21 kbar. The most notable feature is the rapid displacement of these curves to lower temperatures; already at 14 kbar T_c is reduced to one-half its ambient value. Results of the measurements are summarized in Fig. 3, where we plot both T_{c1} and T_{c2} as a function of pressure p for a fixed value of the primary excitation field and frequency. To a first approximation T_{c1} and T_{c2} track each other with increasing p. The initial rate of decrease in T_{c1} is $dT_{c1}/dp = -0.78$ K kbar^{-1}. This is among the strongest depressions of T_c reported. We have checked that the change in T_c is entirely reversible upon decreasing pressure.

Of course, the relevant comparison must be between the volume dependences of T_c. The volume changes (density changes) created by these pressures are not known because the compressibility of K_3C_{60} has not yet been measured. The C_{60}-fullerite is a highly compressible solid (*15*), with a linear compressibility $-d\ln(a)/dp = 2.3 \times 10^{-12}$ cm^2 dyne^{-1}, equal to that of the interlayer compressibility of graphite [$d\ln(c)/dp$]. It could be that K_3C_{60}, with the same crystal type (fcc) and lattice constants as C_{60} (*6, 16*) would be similarly compressible. However, the actual crystal structure adopted is well known from strongly ionic bonding $A_3{}^{+}B^{3-}$ compounds [cryolite structure (*17*)], and the electron is considered to be completely transferred (*10*). These points argue for an ionic crystal of much reduced compressibility.

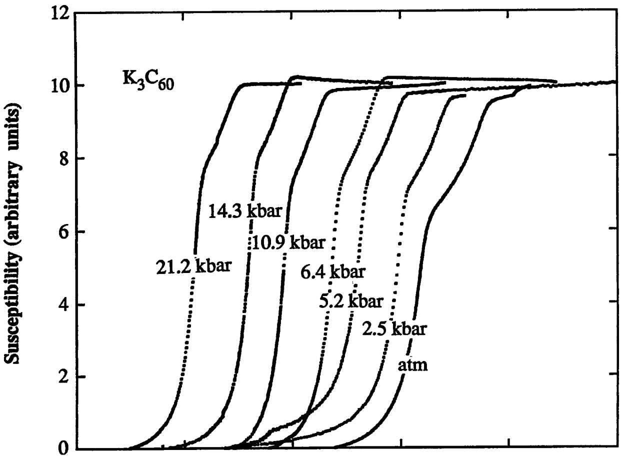

Fig. 2. $\chi(T)$ curves of a pressed sample, as in Fig. 1, at the various pressures indicated. For pressures $2 < p < 10.9$ kbar a small anomaly appears in the temperature range $7 < T < 10$ K that is not understood but also may be due to weak intergranular coupling effects.

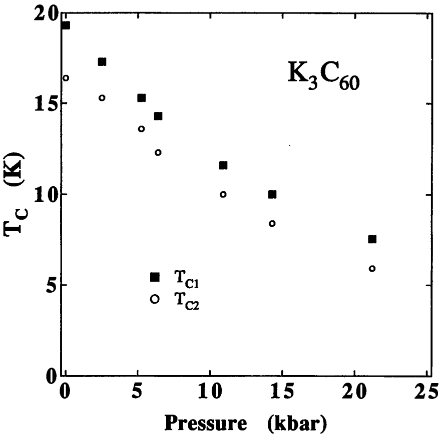

Fig. 3. Dependence of T_{c1} and the (morphology-dependent) T_{c2} on applied pressure, p.

Among A15 compounds with comparable critical temperatures, $dT_c/dp = +0.0241$ and -0.022 K kbar^{-1} for V_3Si (*18*) ($T_c = 16.9$ K) and Nb_3Sn (*19*) ($T_c = 17.9$ K), respectively. This is in contrast to the hole-doped cuprates, which have comparable T_c and κ-parameter to the alkalifullerides, $La_{2-x}(Ba,Sr)_xCuO_4$ in which dT_c/dp ranges (*20*) from near $+0.3$ K kbar^{-1} to as high as $+0.79$ K kbar^{-1} for $La_{1.8}Ba_{0.2}CuO_4$ (*21*). Thus, in absolute magnitude, dT_c/dp in K_3C_{60} is comparable to the Ba-doped cuprates with $T_c = 39$ K, but the sign is opposite. In this latter case, it has been argued (*22*) that dT_c/dp, independent of sign, is greater than allowed by conventional Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity in which electron pairing is mediated by electron-phonon coupling. The other related superconducting family is the organic low-dimensional superconductors, where T_c often shows a maximum as a function of pressure, and dT_c/dp can be as large as -3 K kbar^{-1} at pressures below 1 kbar (*23*).

Recently, Johnson *et al.* (*12*) proposed that superconductivity in K_3C_{60} may arise from cooperative dynamic Jahn-Teller–induced pairing of coupled C_{60} $t_{2u}(p\pi)$ orbitals, leading to a strong increase in T_c with decreasing volume. Simply doubling the overlap from 1 to 2% is predicted to increase T_c from 17 to 30 K. Clearly, our experimental observation of a strong decrease in T_c with pressure is at odds with this theory.

Chakravarty and Kivelson (*11*) have argued that the C_{60} molecule's electronic structure, specifically the partially filled π-electron system, can in itself provide an effective attractive interaction for the electrons, favoring even occupancy of the C_{60} molecules, that is, electron pairing. In the limit where the overlap between C_{60} molecules is weak compared to the pairing energy, a positive pressure dependence is predicted for T_c in opposition to the results presented here. For the reverse situation, overlap comparable to or larger than the pairing energy, then one recovers an essentially BCS-type dependence of T_c on the change in density of states or bandwidths, that is, decreasing T_c under pressure.

Taking the simplest possibility, that superconductivity in K_3C_{60} follows the BCS form, then a strong pressure dependence would develop as follows. In BCS, $T_c \propto \omega \exp(-1/\lambda)$, where ω is a characteristic phonon frequency and λ is the electron-phonon coupling parameter that is linearly proportional to the density of electronic states at the Fermi energy, $N(E_F)$, and inversely proportional to ω^2. Because of the exponential dependence, we expect $\lambda(p)$ to dominate. Recently, we have suggested, on the basis of the measured London penetration depth (*7*) that the structure in the density of states $N(\varepsilon)$ near E_F is unusually narrow, around 600 K wide. Pressure is expected to increase ω and broaden the density of states at E_F, thereby reducing $N(E_F)$, and a relatively strong decrease in T_c could result. Whether this simple model can explain the magnitude of dT_c/dp remains an open question.

The same arguments might be used to explain the higher T_c observed in Rb_xC_{60} (*6, 8*) whose superconducting phase composition and structure remain unknown. Because the Rb^+ ion is larger than K^+, it would likely decrease the density of C_{60} packing, resulting in a narrowing of the band and a further enhancement of the density-of-states at E_F. Further work in progress on the Rb_xC_{60} system to determine the composition, structure, and pressure dependence will answer these questions (*24*).

Note added in proof: Our preliminary measurements on a T_c = 30 K Rb:C_{60} sample show an even larger rate of decrease $dT_c/dp = -1.0$ K kbar^{-1} (*25*).

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Environmental Patterns in the Origins of Higher Taxa: The Post-Paleozoic Fossil Record

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Of the 26 well-preserved orders of benthic marine invertebrates that have originated since the beginning of the Mesozoic, 20 first appear in onshore environments. This distribution differs significantly from that shown by well-preserved genera and families, and by the 16 poorly preserved orders. These discordances suggest that the pattern of preferential onshore origination is not an artifact of preservation or collection and that the origin of higher taxa cannot be regarded as a simple extrapolation of rates and patterns at lower levels. The onshore environment fosters production or enhances survivorship of species that initiate lineages tending to accumulate suites of derived characters and that thus are ultimately afforded high taxonomic rank.

HIGHER TAXA HAVE NOT ARISEN randomly in space and time. For example, most of the skeletonized invertebrate phyla and classes originated in the Early Paleozoic radiations (*1*). Recently, environmental trends have also been recognized, with a variety of Paleozoic (*2*) and post-Paleozoic (*3–6*) marine taxa evidently originating in onshore settings and spreading across the continental shelf; further, a number of taxa today restricted to the outer shelf, slope, or abyssal environment have fossil records suggesting a more onshore distribution earlier in their histories (*3, 7*). Here we test the generality of this pattern with a survey of the environment of first appearance for all known post-Paleozoic benthic marine invertebrate orders. Our results corroborate the environmental bias in originations: 77% of the well-preserved orders first appear in relatively disturbed, onshore environments. This pattern contrasts significantly with the more even pattern seen for first appearances of orders with poor preservation potential and for first appearances of genera within the well-preserved orders. The first disparity suggests that the environmental pattern in well-preserved orders is not an artifact of the stratigraphic record, and the second suggests that major evolutionary novelties arise differently from novelties at the genus level.

As currently recognized, 42 orders of marine benthic invertebrates have originated since the beginning of the Mesozoic. Of these, 16 have skeletons that are too lightly calcified (for example, the notaspidean gastropods) or too readily disarticulated (for example, the eight seastar orders) to yield a reliable record of the time or environment of first occurrences, and these are treated separately from the remaining 26 orders (*8*) (Fig. 1). In the absence of a complete phylogenetic analysis of skeletonized invertebrates, we use ordinal origination as a rough proxy for the origin of important evolutionary novelties, including those giving rise to new body plans (*4, 5, 9*). We are testing for differences across hierarchical levels, not validity of a particular taxonomy, and where

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