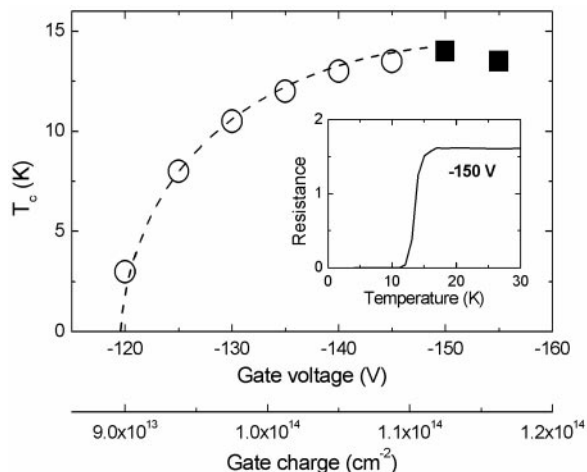


**Fig. 5.** Superconducting transition temperature  $T_c$  as a function of gate bias. A maximum  $T_c$  of 14 K is achieved for a gate bias of  $-150$  V. The gate charge is calculated from the capacitance of the insulating layer and the applied voltage. The inset shows the superconducting transition. The open and solid symbols indicate insulating ( $d\rho/dT < 0$ ) and metallic ( $d\rho/dT > 0$ ) behavior, respectively, above  $T_c$ .



(25). The transition temperature  $T_c$  increases gradually up to a maximum value of 14 K for the highest gate voltages possible (Fig. 5), which is slightly higher than for ladder materials at high pressure (19, 20). The experimental range is limited by the breakdown strength of the  $\text{Al}_2\text{O}_3$  layer. The residual resistivity per ladder plane is slightly less than for bulk single-crystal samples (25), revealing the high quality of the MBE-grown films. In the inset of Fig. 4, a linear dependence of the resistivity  $\rho$  above  $T_c$  can be observed, which is similar to doped two-dimensional cuprates (26). Moreover, note that the temperature dependence above  $T_c$  changes from insulating ( $d\rho/dT < 0$ ) to metallic ( $d\rho/dT > 0$ ) around optimal doping (maximum  $T_c$ ) (Fig. 5). In addition, the superconducting transition shifts to lower temperatures by the application of a magnetic field perpendicular to the field-effect structure. A superconduct-

ing coherence length parallel to the ladder direction of  $40 \text{ \AA}$  can be estimated from the suppression of the superconductivity (27). The observation of superconductivity in this two-leg ladder compound is in accordance with the theoretical prediction that hole doping of such materials should lead to pairing and superconductivity.

Our results demonstrate that field-effect doping is a very powerful technique to study electrical properties as a function of doping-level without inducing structural changes or additional disorder. The study of metal-insulator transitions or superconductivity in  $[\text{CaCu}_2\text{O}_3]_4$  are only some possibilities. We envision that this method can be extended to other ladder compounds as well as other materials in order to search for superconductivity as well as to test theoretical predictions.

## High-Temperature Superconductivity in Lattice-Expanded $\text{C}_{60}$

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$\text{C}_{60}$  single crystals have been intercalated with  $\text{CHCl}_3$  and  $\text{CHBr}_3$  in order to expand the lattice. High densities of electrons and holes have been induced by gate doping in a field-effect transistor geometry. At low temperatures, the material turns superconducting with a maximum transition temperature of 117 K in hole-doped  $\text{C}_{60}/\text{CHBr}_3$ . The increasing spacing between the  $\text{C}_{60}$  molecules follows the general trend of alkali metal-doped  $\text{C}_{60}$  and suggests routes to even higher transition temperatures.

The superconducting properties of various materials can be modulated by the application of an electric field, and a variety of field-effect devices have been studied lately (1–9). We recently demonstrated the switching between insulating and superconducting behavior in single crystals of  $\text{C}_{60}$ . The gate-induced superconductivity is

observed for electron doping (5) as well as hole doping (7). The higher superconducting transition temperature ( $T_c$ ) for hole doping may be ascribed to a larger density of states at the Fermi level and stronger coupling to phonons (8, 10, 11).  $\text{C}_{60}$  is a particularly interesting superconductor because the dominant electron-phonon

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28. We are grateful to Ch. Kloc and C. M. Varma for valuable discussions. One of us (F.C.B.) would like to thank the company WINTICI for financial support.

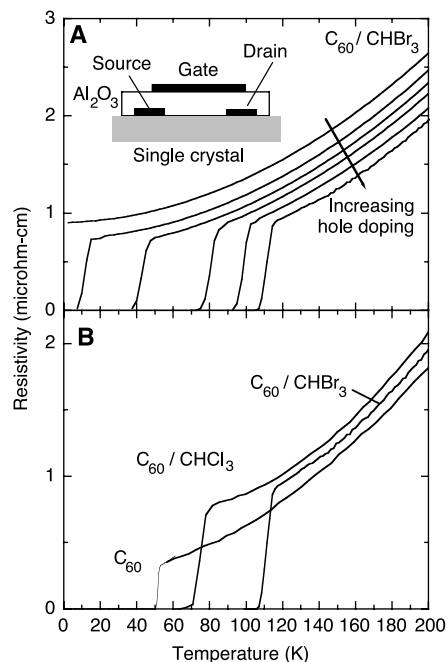
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interaction, being an on-site intramolecular property, can be conceptually separated from the electronic density of states, which is given by the distance between adjacent molecules. Expanding the lattice, therefore, increases the density of states, and the resulting increase of  $T_c$  is well documented in alkali metal-doped bulk samples ( $\text{A}_3\text{C}_{60}$ ) (12, 13). The observation of gate-induced hole doping of  $\text{C}_{60}$ , resulting in a  $T_c$  of 52 K suggests that significantly higher  $T_c$ 's could be anticipated in suitably "expanded"  $\text{C}_{60}$  crystals. Indeed, here we report on raising  $T_c$  to 117 K with such methods.

Undoped  $\text{C}_{60}$  single crystals have been grown from the vapor phase in a stream of hydrogen (14).  $\text{CHCl}_3$  and  $\text{CHBr}_3$  are interca-

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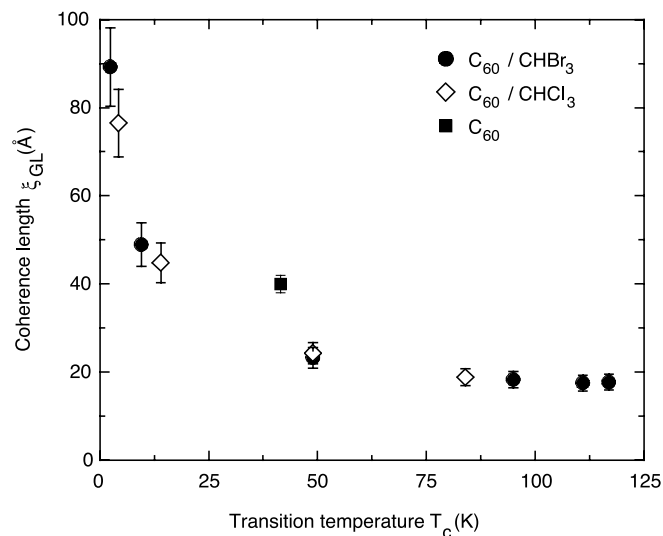
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**Fig. 1.** (A) Channel resistance of a  $C_{60}/CHBr_3$  co-crystal field-effect device as a function of temperature for different hole doping (1.3, 1.6, 1.9, 2.25, 2.7, and 3.2 holes per  $C_{60}$  molecule). The maximum  $T_c$  is at 117 K, and the main drop of the resistance starts at 115 K. The schematic structure of the device is shown in the inset. (B) Comparison of optimum hole-doped  $C_{60}$ , as grown and intercalated with  $CHCl_3$  and  $CHBr_3$ , respectively.

lated into  $C_{60}$  in solution according to (14). The co-crystals exhibit a hexagonal crystal structure. The expansion of the lattice corresponds to a cubic lattice constant of  $\sim 14.28$  and  $14.43$  Å for  $CHCl_3$  and  $CHBr_3$ , respectively (15). Field-effect devices (5, 7) were prepared on growth surfaces of undoped as well as intercalated single crystals (inset of Fig. 1). The observation of ambipolar transport (that is, n- and p-channel activity in intercalated crystals) reveals the absence of severe hole trapping or significant electron doping due to  $CHBr_3$  or  $CHCl_3$ . Nevertheless, the intercalation results in additional disorder as compared with undoped  $C_{60}$  single crystals. This disorder increased the residual resistivity  $\rho_0$ . In the case of electron doping (about three electrons per  $C_{60}$ ),  $\rho_0$  is in the range of 500 to 650 microhm-cm for intercalated crystals as compared with 250 to 300 microhm-cm for undoped  $C_{60}$ . Thus, the resistivity values for intercalated samples are similar to those reported for alkali metal-doped material (7). The doping level of the material is estimated from the gate charge, assuming that only one monolayer takes part in the conduction (5–7).

When the gate voltage in the field-effect device was increased, the charge carrier concentration increased and the temperature dependence exhibited metallic characteristics. When the hole density  $p$  reached approximately one

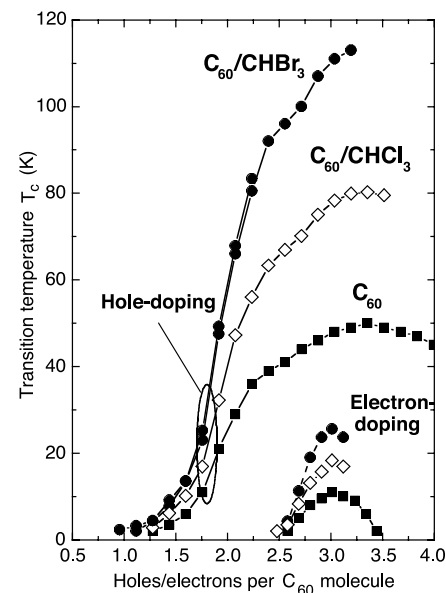


**Fig. 2.** Coherence length as a function of  $T_c$  for hole-doped as-grown and intercalated  $C_{60}$  single crystals. The decrease of  $\xi$  with increasing  $T_c$  is in accordance with theoretical considerations.

hole per molecule, superconductivity above 1.7 K was observed. More holes led to higher values of  $T_c$ , and the value of  $T_c$  depended on the size of the intercalant molecule and  $p$ . The highest  $T_c$  we observed was for  $C_{60}/CHBr_3$  with 3 to 3.5 holes per  $C_{60}$  molecule [with an onset at 117 K and a rapid drop at 115 K (Fig. 1)]. When a magnetic field was applied perpendicular to the metallic layer, the resistive transition shifted to lower temperature, and from the shift, interpreted as the upper critical field  $H_{c2}$ , values for the coherence length  $\xi_{GL}$  were extracted by means of the standard extrapolation (12, 13). A systematic decrease of  $\xi_{GL}$  with increasing  $T_c$  was observed (Fig. 2). This general trend is expected because  $\xi$  is proportional to  $v_f/T_c$ , where  $v_f$  is the Fermi velocity. A more detailed analysis would require that parameters such as the electronic mean free path and density-of-states effects have to be taken into account. In any case, the coherence length at highest  $T_c$  is only approximately two intermolecular distances.

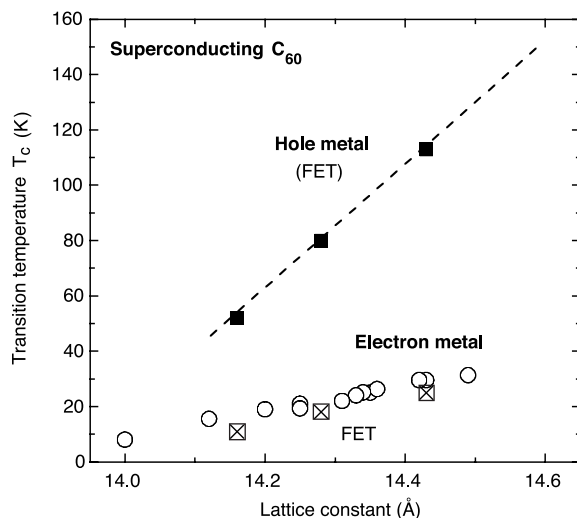
The shape of the carrier concentration dependence of  $T_c$  was similar in samples with or without intercalation (Fig. 3), and this was the case for both electron and hole doping. For electron doping, superconductivity was observed only in the range of  $\sim 2.5$  to 3.5 electrons per  $C_{60}$  molecule, which corresponds to a narrow region around half-filling of the conduction band that is derived from three molecular states. In contrast, a smooth increase of  $T_c$  was observed for hole doping. The maximum was reached between 3 and 3.5 holes per  $C_{60}$ . The upper end of the doping level is given by the electric breakdown strength of the gate oxide. In Fig. 3, all of the data are collected and the scaling of  $T_c$  among the different variants of  $C_{60}$  is evident. Among the hole metals, the  $T_c$  ratios are 2.3:1.6:1 for  $C_{60}/CHBr_3$ – $C_{60}/CHCl_3$ – $C_{60}$ . The same ratios are also found for the respective electron metals, which may be a consequence of changes in the bandwidth and density of states upon intercalation. Density-of-states

effects had been thought to be the main reason for the changes in  $T_c$  in chemically doped  $A_3C_{60}$  (12, 13). When we compare the present results with those data, we find good agreement (Fig. 4). This shows that the structural change from a face-centered cubic to a hexagonal structure does not significantly influence the superconducting properties of the material. The  $T_c$  in the gate-doped materials is slightly lower than expected from the bulk data. This difference might be a consequence of the two-dimensionality of the field-effect structure (5), because the charges at these high densities are confined in



**Fig. 3.** Variation in  $T_c$  as a function of charge carrier density for electron- and hole-doped  $C_{60}$  crystals. Incorporation of  $CHCl_3$  and  $CHBr_3$  expands the lattice, enhances the electronic density of states, and causes  $T_c$  to increase. Holes are doped into the valence band that holds 10 charge carriers per  $C_{60}$  molecule, and electrons are accommodated in the conduction band holding six electrons.

**Fig. 4.** Variation in  $T_c$  as a function of lattice constant for electron- and hole-doped  $C_{60}$  crystals. Square symbols are the present results using gate doping with electrons (open squares) or holes (solid squares). Open circles are for chemically doped  $A_3C_{60}$  bulk samples, where the variation of the lattice parameter is due to the different size of the ions (A).



the topmost layer of the crystal. An approximately linear increase of  $T_c$  with increasing lattice constant was observed for hole-doped intercalation compounds, pointing to a vanishing of  $T_c$  for a lattice parameter of  $\sim 13.9$  to  $14.0$  Å. Recent theoretical considerations are in contrast to this result (16).

The analysis in Fig. 4 suggests that even higher values of  $T_c$  should be achievable. If the lattice parameter can be further increased by  $\sim 1\%$ ,  $T_c$  is expected to exceed 150 K. The question is how to further expand the lattice without finally losing the cohesion. Although

Coulomb forces between the anions and cations provide some additional stability of the  $A_3C_{60}$  crystals, the expansion of van der Waals-bonded  $C_{60}$  with neutral molecules poses new challenges. In this context, the field-effect transistor geometry with the charged layer sandwiched in between the gate dielectric and the bulk of the crystal might provide additional advantages. It is generally thought that superconductivity in  $C_{60}$  is mediated by electron-phonon interaction. In light of  $T_c$  exceeding 100 K, it will be particularly revealing to evaluate the effective Coulomb interaction and the role of nonadiabatic

pairing channels, because the Fermi energy is not much greater than the phonon energy (12, 13, 17, 18).

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## Restricting Dislocation Movement in Transition Metal Carbides by Phase Stability Tuning

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A mechanism to enhance hardness in multilayer coatings is proposed. Using the technologically important hard transition metal carbides as prototypes, although the principle is transferable also to other systems, we demonstrate, from first-principles calculations, that by suitable alloying the energy difference between several competing structures in the transition metal carbides is small or tunable. This creates multiphase/polytypic compounds with a random or controllable layer stacking sequence, systems in which the propagation of dislocations can be strongly suppressed by a large number of interfaces between structures with different glide systems, accordingly allowing the possibility of a greatly enhanced hardness. With modern thin-film technologies, it should therefore be possible to deposit such materials that will express multilayer characteristics with only minor changes in the chemical constitution of the material, which is in contrast to conventional superlattices.

Hardness is one of the most sought after material properties and one of the most important attributes of the transition metal carbides and nitrides. Hardness is important for many obvious reasons, reducing the wear of everyday objects being one and

creating machining tools being another. In materials science, one distinguishes between the hardness and the strength of a material. Strength is the resistance of a material against failure, here separated into brittle and ductile failure, whereas hardness

is the resistance against localized plastic deformation, microscopically corresponding to the motion of dislocations. The hardness of a material, often measured by indenter techniques, is therefore determined by how resistant the bonds in the material are against distortions and how dislocations are able to move in the system (1). A hard material should ideally also be ductile to maximize potential use.

In recent years, the search for novel hard materials has benefited from advances in the theoretical treatment of electronic structure in solids. The hardness of a material is not entirely given by the electronic structure readily available from density functional theory calculations, but the first factor, the straining of bonds in a material, can be modeled theoretically by calculating the elastic constants of the material.

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