Evidence Suggesting Superconductivity at 250 K in a Sequentially Deposited Cuprate Film

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An artificial cuprate compound belonging to the BiSrCaCuO family with eight adjacent CuO_2 layers in each building block was deposited on a single crystal of $SrTiO_3$ by sequentially imposed layer epitaxy. This compound undergoes a five order of magnitude resistivity drop with an onset near 280 kelvin and an offset at 250 kelvin. It exhibits a diamagnetic variation of susceptibility and magnetization below 290 kelvin. Additional observed features, such as strongly nonlinear conductivity, suggests superconductivity as a plausible explanation of the properties of this compound.

The maximum critical temperature T_c that can be reached with a superconducting cuprate is still an open question. After the discovery of YBaCuO in 1987, higher values of T_c have been observed in new cuprate compounds exhibiting the well-known sequence of atomic layers $BM_rB(CuO_2/Ca)_{n-1}CuO_2$, usually referred to as the $[r^2(n-1)n]$ compound of the cuprate family M, where usually B is Sr or Ba and M is Bi, Tl, or Hg. In 1988, the [2223] compound of the Tl family (*1*) reached 125 K, the record that held for 5 years until 1993 when the [1223] compound of the Hg family was shown to exhibit a superconductive transition at 133.5 K under atmospheric pressure (*2*) and 164 K under high pressure (*3*). These compounds are elaborated as bulk or film samples by conventional techniques, that is, the thermodynamical and chemical conditions were adjusted in order to perform the crystal growth in a region of the phase diagram where the compound is stable. For $n = 1$, 2, and 3, T_c is clearly an increasing function of n. However, until now these techniques did not allow the making of pure $[r2(n-1)n]$ phases with $n > 3$, which are suspected to be unstable at least at high deposition temperatures.

Artificial layering of cuprates with $n > 3$ was thus used by different teams in two main research directions. First, since 1987 different teams have attempted to make $ResCa_{n-1}Cu_nO_x$ with $n > 3$ (where Res stands for different types of charge reservoir blocks), either by ion beam deposition (*4*), by conventional molecular beam epitaxy with Knudsen and electron gun sources (*5*), or by laser ablation (*6*). Although the growth and the structural properties of such films with values of n up to 10 were actually described, few transport measurements have been reported as a function of n (*7*). The quality of the obtained phases was probably not sufficient for proposing an answer to the following question, "Does a special value of n correspond to a maximum T_c?". A second research route corresponds to the attempts to synthesize the "parent" layered phase $CaCuO_2$ currently called the infinite layer phase (*8*) corresponding to $n \rightarrow \infty$. More generally, phases of the family $(A_{1-x}B_x)_{1-y}CuO_2$ were made by different teams. Superconductivity was first observed in bulk materials (*9*) of this family, prepared at temperatures in the range of 1000°C under high pressure. Azuma *et al.* (*10*) have shown that T_c of a compound where A is Sr, B is Ca, $x = 0.3$, and $y = 0.1$ could reach a T_c of 110 K. The microstructure of these compounds as studied by high-resolution transmission electron microscopy (*11*) shows that the superconducting behavior is always associated with the presence of defects in intergrowth with the infinite layer phase. One explanation could be that these lamellar or loop-like defects (*12*) play the role of "charge reservoir" and are possibly required in order to dope the infinite layer phase. Recently, a new family of copper oxide compounds (*13*) was also observed to be superconductive near 100 K.

Films of infinite layer phase were also deposited by sputtering (*14*), by metal-organic chemical vapor deposition (*15*), or by laser ablation (*16*, *17*). Only one team used layer-by-layer deposition with a laser ablation process, and only this team reported signs of superconductivity above 100 K in the case of the $Sr_{1-x}Ca_xCuO_2$ phases (*18*), but no zero resistance was observed and the amount of superconductive phase was found to be small. All the other teams, who used continuous deposition, observed a semiconducting behavior of these films. However, recently a small sign of resistive transition was observed at 185 K in a $Sr_{1-x}CuO_2$ phase (*19*) deposited by conventional laser ablation with a substrate temperature of 550°C. We report the transport properties of an artificial cuprate compound belonging to the BiSrCaCuO family, deposited atomic layer by atomic layer on (100) $SrTiO_3$. The number n of CuO_2 layers in each building block is eight.

The film was grown by the sequentially imposed layer epitaxy, using a technique derived and modified from the process already described in detail (*20*). The deposition chamber is the EVA32 equipped with the commercial atomic oxygen plasma source (OPS) from RIBER (*21*). During the deposition, the local atomic pressure near the sample was kept to 5×10^{-5} torr and the substrate temperature was fixed at 500°C. Bismuth, strontium, and calcium were deposited from Knudsen cells, and the copper was evaporated from an electron gun. The surface structure of the film was monitored in real time with a 35-keV reflection high-energy electron diffraction (RHEED) gun. The oscillations of the RHEED intensity were used to stop the

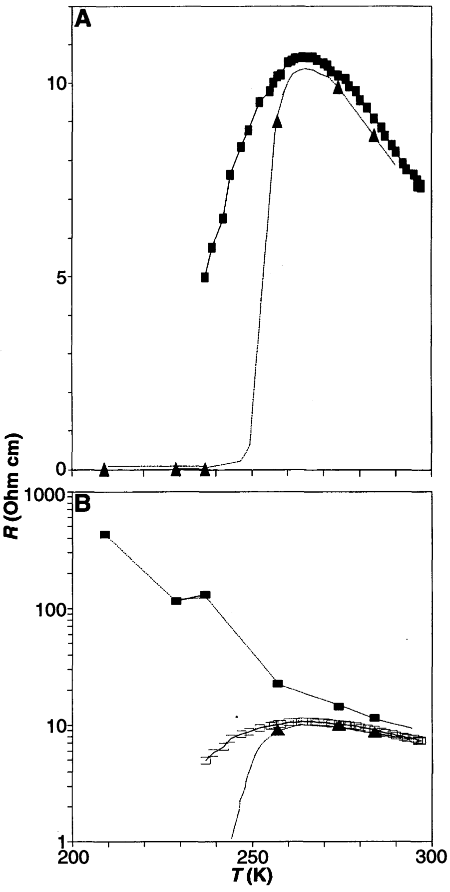

Fig. 1. Resistivity of the film versus temperature (**A**) with a current of 10^{-8} A (■) and with a current of 10^{-9} A (▲ and ---). (**B**) The same result in log-scale with addition of the resistivity measured for a current of 10^{-7} A (□).

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deposition of each atomic layer when a maximum was reached. We observed for the growth of the 2201 phase (*17, 22*) that the sticking coefficients of the different species changed drastically during the first 5 nm of deposition. Thus the deposition sequence had to be adjusted for the first tens of atomic layers. A deposition sequence controlled by computer was then used to complete the film thickness up to ~30 nm. The distance between adjacent CuO_2 layers was measured to be 0.338 nm by x-ray diffraction. The superconducting phase was observed to be mixed with a secondary insulating phase. The detailed composition and structure of the superconducting phase remains to be determined.

Contacts were made from silver paint to allow the measurement of the dc resistivity by the four-point technique. The film resistivities for a current of 10^{-8} and 10^{-9} A are shown in Fig. 1A, and Fig. 1B presents on a logarithmic scale these values and the resistance measured with a current of 10^{-7} A. The measurements for currents of 10^{-9} and 10^{-7} A were extracted from full current-voltage (*I-V*) characteristics measured at 208, 229, 235, 257, 275, and 284 K. The *I-V* characteristics measured at 235 and 284 K are shown in Fig. 2, A and B, respectively. At 235 K, the *I-V* behavior clearly shows a region where the resistance goes below the sensitivity limit of the equipment. This region shows a critical current of ~10 mA/cm^2 and disappears at temperatures above 250 K. At 229 K and at 208 K, the low-current part presents a slightly negative slope, probably related to the high resistance of the contacts. The onset of the transition is observed between 270 and 280 K. At 208 K, the low-current resistivity of the film is <1 ohm cm^{-1} (the limit of sensitivity of the equipment), whereas the normal resistivity for a large current is >100 ohm cm^{-1} (Fig. 1B), a decrease of more than five orders of magnitude. This measurement was made several weeks after the sample was prepared. The general features are reproducible but deteriorate slowly. After an additional 2 weeks the sample was structurally stable with a resistive transition over 200 K. Resistive transitions in the same temperature range have been subsequently observed on the only two other samples of the same type. Two other samples with different *n* values show transitions of 130 K and 165 K.

The magnetic properties of a small piece broken from the first sample (volume 5×10^{-8} cm^3) was measured both by ac susceptibility and on a Quantum Design superconducting quantum interference device (SQUID). The ac susceptibility measurement upon cooling shows a diamagnetic effect below 290 K (Fig. 3A). This effect is small and does not show a good reproducibility in intensity, but corresponds always to a negative magnetization. The variation of the magnetization versus temperature during a field cooling at 0.2 T measured with a SQUID is presented in Fig. 3B. The analysis is strongly hampered by the procedure of sample holder and substrate subtraction, which presently limit the overall sensitivity to 10^{-7} emu. The observed value of the diamagnetic transition (Fig. 3B) is very close to the sensitivity limit of the equipment, and it should be interpreted with caution. The measured variation of the magnetization corresponds roughly to an upper limit of 2×10^{-7} emu. This value leads typically to a Meissner fraction of the order of 10%, if the value of H_{c1} is in the range of hundreds of Gauss. A search for a diamagnetic hysteresis cycle was also systematically performed at various temperatures with the same sensitivity limitations. The result below 250 K is consistent with a magnetization variation of the same order of magnitude.

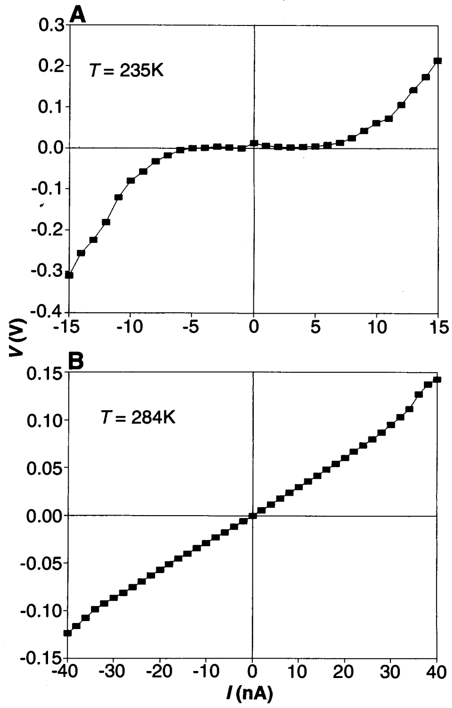

Fig. 2. Current-voltage characteristics measured at (**A**) 235 and (**B**) 284 K.

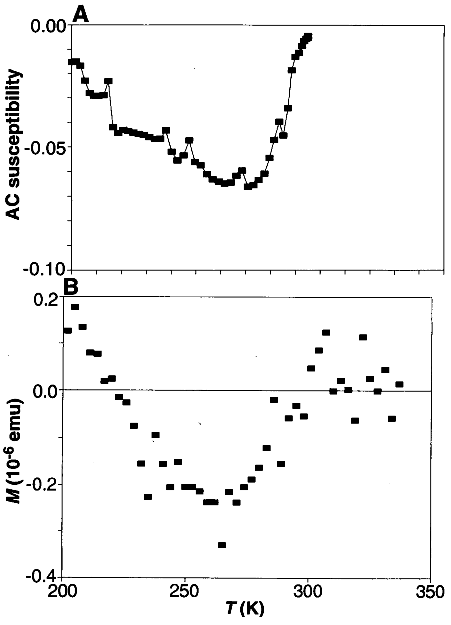

Fig. 3. (**A**) Variation of the ac susceptibility upon cooling and (**B**) variation of the magnetization versus temperature during a field cooling at 0.2 T measured with a SQUID.

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23. We acknowledge G. Deutscher for numerous useful and encouraging discussions during the past 6 years. We also thank N. Bontemps and P. Monod for the magnetization measurements and P. Luzeau for the MBE deposition equipment.

18 November 1993; accepted 22 November 1993

The Transition State of the F + H_2 Reaction

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The transition state region of the F + H_2 reaction has been studied by photoelectron spectroscopy of FH_2^-. New *para* and *normal* FH_2^- photoelectron spectra have been measured in refined experiments and are compared here with exact three-dimensional quantum reactive scattering simulations that use an accurate new ab initio potential energy surface for F + H_2. The detailed agreement that is obtained between this fully ab initio theory and experiment is unprecedented for the F + H_2 reaction and suggests that the transition state region of the F + H_2 potential energy surface has finally been understood quantitatively.

The transition state plays a central role in chemical reaction dynamics (*1*). Asymptotically observable quantities such as integral cross sections and thermal rate constants often depend crucially on what happens in a relatively narrow region around the transition state saddle point, and a number of approximate and exact theories of bimolecular exchange reactions exploit this (*2*). It is therefore particularly interesting if an experiment can be devised to look directly at the transition state, without having to infer what happens there from asymptotic measurements. The photoelectron spectroscopy of stable negative ions such as FH_2^- is one such experiment that has been developed recently at Berkeley (*3*). In favorable circumstances, when the equilibrium geometry of the anion lies close to the neutral transition state, the photoelectron spectrum of the anion can give a direct vibrationally resolved picture of the transition state dynamics and so realize the goal of "transition state spectroscopy."

The circumstances are particularly favorable for FH_2^-, which photodetaches close to the transition state of one of the most thoroughly investigated reactions in chemical dynamics. Various aspects of the (asymptotic) product energy and angular distributions of the F + H_2 reaction have been measured in chemical laser (*4*), infrared chemiluminescence (*5*), and crossed molecular beam experiments (*6*), for example, and accurate thermal rate constants have been obtained over a large temperature range (*7*). The reaction has also played a key role in the development of quantum reactive scattering theory, with its high exoergicity, unsymmetrical mass combination, pronounced resonance structure, and experimental accessibility all making it a prime target for study (*8*). Moreover, the challenges posed by the transition state region of the F + H_2 potential energy surface (PES) have long made it a favorite problem in electronic structure theory (*9*), and numerous global F + H_2 potential energy functions have been proposed (*10, 11*).

Given this background and encouraging early work on the FH_2^- system by Zhang and Miller (*12*) and Weaver and Neumark (*13*), four of the present authors have recently completed a detailed experimental and theoretical study of the FH_2^- photoelectron spectrum (*14*). Experiments were performed in this study for both *para* and *normal* FH_2^-, that is FH_2^- ions prepared by clustering F^- with both *para* and *normal* hydrogen, and three previously proposed semiempirical F + H_2 PESs (*11*) were used in quantum mechanical simulations of the resulting spectra. (Recall that in *para* H_2 only the even rotational levels are populated, whereas in *normal* H_2 the odd:even population ratio is 3:1.) The study succeeded in showing that the *para* and *normal* FH_2^- photoelectron spectra are dominated by bending progressions associated with the F + H_2 transition state region and are therefore highly sensitive to the details of the F + H_2 bending potential in this region. None of the three F + H_2 PESs used in the quantum dynamics simulations was particularly successful, however, in giving a truly quantitative prediction of the experimental spectra (*14*).

The inadequacies of the semiempirical surfaces suggest that a better approach is to construct a fully ab initio PES for F + H_2, which has proved a considerable challenge. The main problem is that both the classical barrier height and the bending potential at the transition state are highly sensitive to electron correlation, and very large orbital and configuration basis sets are required if they are to be converged to chemical accuracy (*9, 15, 16*). However, a recent benchmark full configuration interaction (CI) calculation by Knowles *et al.* (*15*) and systematic studies of the convergence of the topology of the FH_2 transition state with respect to the orbital basis and electron correlation treatment (*16*) have shown that the barrier height and reaction exothermicity can now be obtained to sufficient accuracy for dynamics calculations. Calculations at this level of convergence are highly sophisticated and require the use of very large orbital basis sets, extended internally contracted multireference CI (MRCI) wave functions (*17*) with complete active space self-consistent field (CASSCF) reference functions (*18*), and application of the Davidson correction (*19*) for the effect of higher excitations (MRCI + Q). Nevertheless, because the barrier height and reaction exothermicity are sensitive to very different regions of the PES and yet are obtained with comparable (0.1 kcal/mol) accuracy (*15, 16*), and because the MRCI + Q calculations are efficient enough to be performed at a large number (~600) of other geometries, a globally accurate F + H_2 PES is promised by this same level of theory. Such a highly correlated ab initio PES for F + H_2 has recently been constructed by two of the present authors (*16*), and the remainder of this report provides the first stringent experimental test of this new surface by comparison with the *para* and *normal* FH_2^- photoelectron spectra.

A two-dimensional cut through the transition state region of the new F + H_2 PES as a contour diagram is shown in Fig. 1, with contours of the *para* FH_2^- vibrational ground state wave function superimposed. The anion wave function is calculated in the harmonic normal mode approximation (*12*) and the best available equilibrium geometry ($R_{\text{F-H}_2}$ = 2.075 Å, $r_{\text{H-H}}$ = 0.770 Å, and $\gamma = 0°$) and vibrational frequencies ($\omega_1 = 292$ cm^{-1}, $\omega_2 = 773$ cm^{-1}, and $\omega_3 = 4143$ cm^{-1}) from the ab initio calculations of Nichols *et al.* (*20*) are used. The corresponding *ortho* wave function may be obtained by reversing the sign of one of the two lobes and is degenerate with the *para* wave function in Fig. 1 (*14, 16*).

The key features of the *para* and *normal* FH_2^- photoelectron spectra are already implicit in Fig. 1. The first thing to notice is that the anion wave function has a good

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