positions contains Nb of valence 4 with a localized $4d^1$ configuration, giving rise to the magnetism, and other sites contribute delocalized electrons, giving rise to the conductivity. Antiferromagnetism and conductivity in $Nb_{12}O_{29}$ could therefore be analogous to ferromagnetism and superconductivity in materials such as $ErRh_4B_4$, involving different subsets of electrons.

Our evidence shows that $Nb_{12}O_{29}$ is a metallic antiferromagnet with an ordering temperature of 12 K. The resistivity measurements indicate that it is metallic but not superconducting down to 0.25 K. To the best of our knowledge, it is the first niobium-oxide-based magnetic material. The mixed dimensionality of the crystal structure apparently affects the magnetic properties through the reduction of the true ordering temperature to half of θ_{CW}. We have found that the oxides $Nb_{25}O_{62}$, $Nb_{47}O_{116}$ and $Nb_{22}O_{54}$ derived by reduction of Nb_2O_5 also display Curie-Weiss behaviour in plots of χ against T, but do not magnetically order down to 2 K. Their θ_{CW}s of 0, 7 and 12 K indicate the increasing strength of antiferromagnetic interactions as the Nb^{4+} content increases. Thus, antiferromagnetic interactions are a general property of reduced Nb oxides with crystallographic shear structures. Although some reduced Ti and V oxides based on $3d$ shells are antiferromagnetic[12], $4d$- and $5d$-based reduced Mo and W oxides do not display any tendency towards local-moment magnetism. The occurrence of such local moments in reduced Nb $4d$-based oxides suggests the existence of narrower electronic bands and poorer metal-oxygen covalency than occur in their molybdenum and tungsten oxide counterparts. Further research is necessary to determine the degree of localization of the magnetic states. More detailed study of the magnetic niobium oxides will be of interest in its own right, and may shed light on the relationships between ferroelectricity, antiferromagnetism and covalency in transition metal oxides. □

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Superconductivity at 18 K in potassium-doped C_{60}

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THE synthesis of macroscopic amounts of C_{60} and C_{70} (fullerenes)[1] has stimulated a variety of studies on their chemical and physical properties[2,3]. We recently demonstrated that C_{60} and C_{70} become conductive when doped with alkali metals[4]. Here we describe low-temperature studies of potassium-doped C_{60} both as films and bulk samples, and demonstrate that this material becomes superconducting. Superconductivity is demonstrated by microwave, resistivity and Meissner-effect measurements. Both polycrystalline powders and thin-film samples were studied. A thin film showed a resistance transition with an onset temperature of 16 K and essentially zero resistance near 5 K. Bulk samples showed a well-defined Meissner effect and magnetic-field-dependent microwave absorption beginning at 18 K. The onset of superconductivity at 18 K is the highest yet observed for a molecular superconductor.

The sensitivity to air of alkali-metal-doped fullerenes (A_xC_n) limits the choice of sample preparation and characterization techniques. To avoid sample degradation, we carried out reactions with the alkali metal vapour and C_{60} in sealed tubes either in high vacuum or under a partial pressure of helium. The C_{60} was purified by chromatography[1] of fullerite[2] and was heated at 160 °C under vacuum to remove solvents.

Small amounts of the individual fullerenes (~0.5 mg) were placed in quartz tubes with alkali metals and sealed under vacuum. These samples were subjected to a series of heat treatments and tests for superconductivity by 9-GHz microwave-loss experiments[5]. Preliminary tests indicated that only the K-doped C_{60} showed a response consistent with a superconducting transition (Fig. 1). For this reason, together with the fact that K_xC_{60} showed the highest film conductivity[1], we focused our studies on the K-doped compound.

The conductivity measurements were performed on potassium-doped films of C_{60} that were prepared in a one-piece all-glass version of the apparatus described previously[4]. This reaction vessel was sealed under a partial pressure of helium before reaction. This configuration allowed both *in situ* doping and low-temperature studies of thin films. All measurements were made in a four-terminal Van der Pauw configuration using a 3-μA a.c. current at 17 Hz. Figure 2 shows the temperature dependence of the resistivity of a 960-Å-thick K_xC_{60} film. The film was doped with potassium until the resistivity had fallen to 5×10^{-3} Ω cm. The resistivity increases by a factor of two on cooling the sample to near 20 K. Below 16 K, the resistivity starts to decrease; zero resistivity ($<10^{-4}$ of the normal state) is obtained below 5 K. The 10–90% width of the transition is 4.6 K. At 4 K we measured the lower bound to the critical current to be 40 A cm^{-2}.

A bulk polycrystalline sample of nominal composition K_3C_{60} was prepared by reaction of 29.5 mg of C_{60} with 4.8 mg potassium. The amount of potassium was controlled volumetrically by using potassium-filled pyrex capillary tubing cut to size in a dry box. The reaction was run with the C_{60} in a 5-mm fused silica tube joined to a larger tube in which the potassium-containing capillary was placed. The tube was sealed after being evacuated and refilled with 10^{-2} torr of helium to serve later as a thermal-exchange gas for low-temperature measurements. With the C_{60}-containing end of the tube at room temperature,

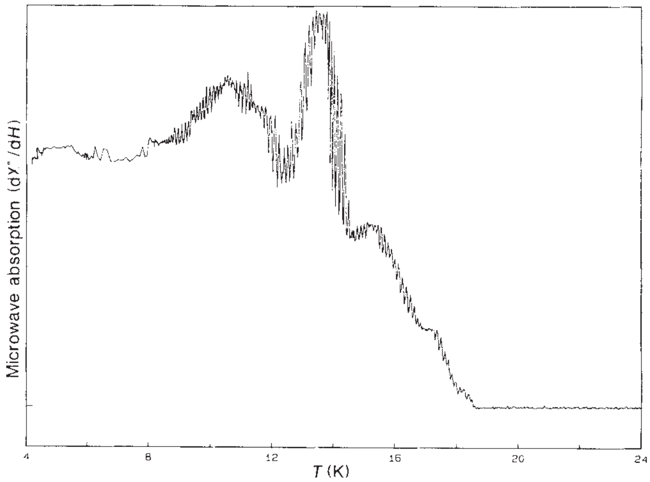

FIG. 1 Microwave loss as a function of temperature for K_xC_{60} in a static field of 20 Oe.

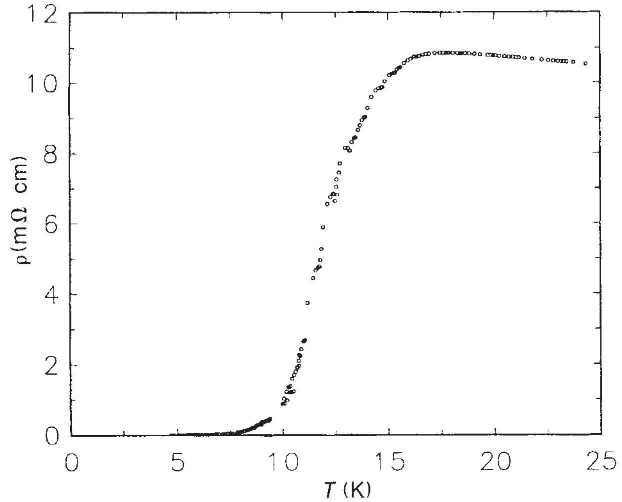

FIG. 2 Temperature dependence of the electrical resistivity of a 960-Å-thick film of K_xC_{60}.

the potassium was distilled from the capillary in a furnace at 200 °C. Some reaction of the potassium with the quartz tube, visible as a dark brown discoloration, was observed at this temperature. Unreacted potassium was observed after this period. Following distillation of the potassium to the C_{60} end, the tube was shortened by sealing to about 8 cm and heated to 200 °C for 36 h. Finally, the tube was resealed to a length of about 4 cm for magnetic measurements.

The temperature dependence of the d.c. magnetization of the sample with nominal composition K_3C_{60} was measured in a SQUID magnetometer (Fig. 3). On zero-field cooling the sample to 2 K, a magnetic field of 50 Oe was applied. On warming, this field is excluded by the sample to 18 K; this verifies the presence of a superconducting phase. The bulk nature of superconductivity in the sample is demonstrated unambiguously by cooling in a field of 50 Oe. A well defined Meissner effect (flux expulsion) develops below 18 K. The shape of the magnetization curve, in particular the temperature-independent signal at low temperature, indicates good superconducting properties for this sample. Also noteworthy is the relatively narrow transition width. The magnitude of the flux exclusion for the zero-field-cooled curve corresponds to 1% volume fraction. This small fraction is possibly due to non-optimal doping or the granular nature of the sample. The large value of the Meissner effect for the field-cooled curve relative to the total exclusion, however,

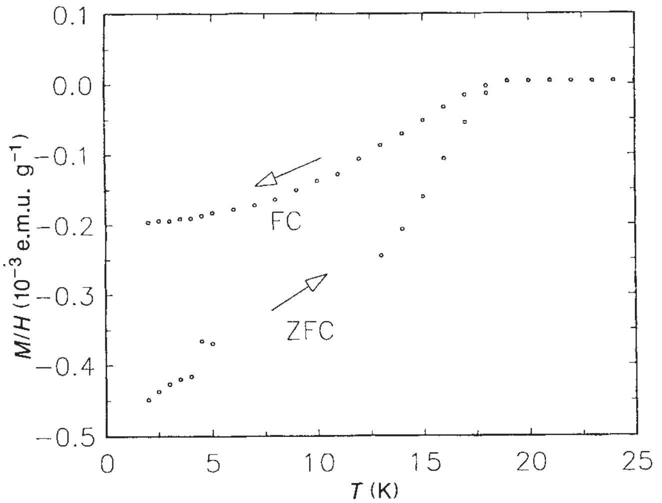

FIG. 3 Temperature dependence of the magnetization of a K_xC_{60} crystalline sample. The direction of temperature sweep in the field-cooled (FC) and the zero-field-cooled (ZFC) curves is indicated by the arrows.

indicates bulk superconductivity in the electrically connected regions.

The universally accepted tests for superconductivity, namely a transition to zero resistance and a Meissner effect showing the expulsion of magnetic field, demonstrate unequivocally the existence of superconductivity in K_xC_{60}. The 18-K transition temperature is the highest yet reported for a molecular superconductor. This may be compared with the previously reported occurrence of superconductivity at 0.55 K in potassium-intercalated graphite[6]. We expect that optimization of composition and crystallinity will lead to further improvement in the superconducting properties. □

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Sedimentation rates, residence times and radionuclide inventories in Lake Baikal from ^{137}Cs and ^{210}Pb in sediment cores

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RADIONUCLIDES in lake sediments may act as indicators of the sedimentation rate of particles on which they are adsorbed; these rates in turn provide a direct indication of the residence times of particles in the water column. The radionuclide ^{137}Cs is anthropogenic (an atomic-bomb product), so that its concentration in sediments also reveals the input history of this species and thus a record of atmospheric contamination by this nuclide in the lake's watershed. Here we report measurements of ^{137}Cs and the natural radionuclide ^{210}Pb in cores from several stations throughout the three basins of Lake Baikal. The results confirm earlier indirect estimates[1] of the mean sedimentation rate, and show that the effective settling rate of these radionuclides is the same as that in the Great Lakes; the longer residence times for Lake Baikal are therefore simply a consequence of its greater depth. As well as allowing estimates of fluxes at the sediment–water interface[2–4], our results provide information on the timing of palaeolimnological events[5], on the existence of different depositional zones throughout the lake, on the long-term (decadal) diffusion of nuclides in sediments[6] and for the development of mass-balance models for sediments and contaminants[7–9].

Caesium-137 and lead-210 (half lives of 30.2 and 22.3 years, respectively) have been measured in 10 sediment cores collected from throughout Lake Baikal (Fig. 1). Each ^{210}Pb profile (Fig. 2) shows a layer of constant activity (surficial mixing) followed by an exponential decrease in concentration with depth to a constant value maintained by *in situ* decay of ^{226}Ra (ref. 2).