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Large magnetoresistance in intercalated Cu oxides

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Magnetism and electrical resistance as a function of magnetic field, temperature, and chemical composition are studied in Cu oxides intercalated with metal phthalocyanines MPc, where M is Fe or Ni, and Pc is $C_{32}H_{16}N_8$. An unusually large positive magnetoresistance (MR) of $\sim$1200% is observed in FePc-intercalated $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ samples with two Cu-O layers in the unit cell ($n=2$). The magnitude of the MR decreased to 40% and $\sim$0% in the FePc-intercalated $n=3$ and $n=4$ samples, respectively, and to $\sim$300% in the NiPc-intercalated $n=2$ sample. [S0163-1829(97)07846-6]

I. INTRODUCTION

An unusually large magnetoresistance (MR) defined as $\mathrm{MR}=R(H)-R(0)/R(0)$, where R is the sample's resistance and H is an external magnetic field, was observed in metallic multilayer films and Mn-based oxides with perovskite crystal structure (see Ref. 1 for a recent review). Physical mechanisms, as well as typical values of a large MR in multilayers and in Mn oxides are believed to be different, and the phenomenon is called either GMR (giant magnetoresistance) or CMR (colossal magnetoresistance), when referring to multilayers or Mn oxides, respectively. Both GMR and CMR are attracting great attention due to interesting basic physics as well as the highly promising technological applications, e.g., in magnetic recording.

In this work, we report the observation of a large MR on the order of 1200% in a new system, that is, the intercalated high-T_c Cu oxides. The effects of chemical composition, as well as temperature and magnetic field on dc magnetization and dc resistance are investigated and discussed. In contrast to most multilayer and Mn-oxides samples, where with application of a magnetic field the resistivity is *decreasing* (negative MR), in our system the resistivity is *increasing* (positive MR). Another important feature of our system is that the magnetic layers are created through vapor phase intercalation (diffusion) of organic molecules containing magnetic ions into a preexisting nonmagnetic metallic host (Cu-oxide crystal). We believe that this work may open up a new approach to creating large MR materials by intercalating other preexisting metallic layered host solids with magnetic guest species.

High-temperature superconducting Cu oxides have a layered crystal structure and some of them, such as BISCO ($Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, where $n=1$, 2, or 3, is the number of Cu-O layers in the unit cell) can be intercalated with various atomic and molecular species bringing about a dramatic modification of the superconducting and normal-state properties.[2–6] In particular, intercalation of the BISCO $n=2$ with metal phthalocyanines, MPc (where M is Fe or Ni, and Pc is $C_{32}H_{16}N_8$) has been shown to give rise to two new crystal structures with the **c** axis expanded by 0.305 or 0.431 nm in $(M\mathrm{Pc})_x$BISCO with $x=0.05$ or 0.1, respectively.[4] A combination of x-ray powder diffraction, scanning tunneling microscopy and spectroscopy (STM/STS), optical absorption and reflection, Fourier transform (FT) infrared (IR) and far IR, micro-Raman scattering, and electron spin resonance (ESR) data has indicated that MPc molecules were inserted between the double Bi-O layers, forming organic monolayers separating the unit cell blocks of the host oxide.[4–7] According to the STM/STS data, the intercalated MPc layers were electrically insulating, but they have been shown to play an important role in determining magnetic properties of the intercalated samples.[4,7]

Hence, using intercalation, one can create crystal structures where electrically conducting layers (such as Cu-O layers) are alternating with magnetic layers (such as the FePc molecular layer). Electronic coupling between the Cu-O layers along the **c** axis will be strongly dependent on scattering of conduction electrons in the MPc layers which, in its turn, depends on the sign and magnitude of both intralayer and interlayer exchange between transition metal ions contained in the intercalated MPc molecules. The exchange interaction is a complex function of concentration, intralayer geometry and the particular type of magnetic ion in MPc, distance between the intercalated MPc layers, as well as electronic structure of a host Cu oxide. In this work, we attempted to study the effect of varying some of these factors (e.g., particular M in MPc, number of layers in the unit cell of host Cu oxides) on magnetic and electrical properties of the samples.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The BISCO ($n=2$, $n=3$) and $CuBa_2Ca_3Cu_4O_{10.5}$ ($n=4$) samples with $T_c\sim$94, 108, and 115 K, respectively, were

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prepared by the standard solid-state reaction. A BISCO $n=2$ powder was exposed to vapors of FePc at 820 K in a 10^{-3} Torr vacuum for several days to produce intercalated FePc_x(BISCO $n=2$) sample. The fact of intercalation could be established from the x-ray powder diffraction, elemental analysis, and weight uptake data (see Ref. 4 for the details). The x-ray diffraction patterns of the intercalated pressed pellets indicate that the desired $x=0.1$ ($\mathbf{c}=1.971\,\mathrm{nm}$) phase was formed only within $\sim 10\ \mu\mathrm{m}$ layer of the surface, while the interior part was the nonmagnetic insulating $x=0.05$ ($\mathbf{c}=1.845\,\mathrm{nm}$) phase. The energy dispersive x-ray spectroscopy (Hitachi) results indicated a fairly homogeneous distribution of Fe, Bi, Sr, Ca, and Cu over the surface of the pellets. To obtain a pure $x=0.1$ phase for magnetic studies, a finely grounded powder of BISCO $n=2$ with grain size below $\sim 10\ \mu\mathrm{m}$ was used for the intercalation. The same treatment procedure as described above was used to produce MPc-intercalated BISCO $n=3$ and $\mathrm{CuBa_2Ca_3Cu_4O_{10.5}}$ samples with three and four Cu-O layers in the unit cell, respectively. The commercially (Aldrich) available samples of MPc ($M=$Fe, Ni, Pb, or $\mathrm{H_2}$) were purified by vacuum sublimation before use. The mixed-metal $(\mathrm{Fe}_x M_{1-x})$Pc samples were prepared by vacuum cosublimation of corresponding amounts of purified FePc and MPc.

Measurements of dc magnetization were carried out with a Quantum Design SQUID magnetometer. dc resistance (R) of the samples was measured by attaching four copper wires to the surface of a pressed pellet bar with a silver paste, arranged linearly at equal distances from each other. Resistivity (ρ) was calculated as $\rho=(\pi t/\ln 2)R$, where t is the thickness of the conducting surface layer. The longitudinal MR was measured using the same four-probe arrangement and a superconducting 12 T magnet. The measurements taken with the reversed polarity of the magnets have shown that the response was symmetrical with respect to the direction of the external magnetic field.

III. RESULTS AND DISCUSSION

A. Magnetic properties

Before intercalation, the superconducting BISCO $n=2$ samples exhibited weak, almost temperature-independent paramagnetism in the normal state. The superconductivity was totally suppressed upon the intercalation, but instead, the $(\mathrm{FePc})_{0.1}$ (BISCO $n=2$) samples exhibited complex magnetic properties. A sharp drop of the zero-field-cooled (ZFC) magnetization and concomitant sharp increase of a divergence between the ZFC and the field-cooled (FC) magnetizations were observed at $T_0 \sim 130\,\mathrm{K}$ (Fig. 1). The magnetization vs field curves were ferromagnetlike with saturation magnetization ~ 0.5 emu/g. They retained the ferromagnetic character up to about 750 K, and became linear upon further heating, indicating transition to a paramagnetic state. These curves were almost identical at 140 and 280 K, but they changed notably below 130 K. In particular, both remanent magnetization and coercive field exhibited a sharp increase (inset, Fig. 1), and the FC values of magnetization became strongly dependent on the thermomagnetic history of the sample.

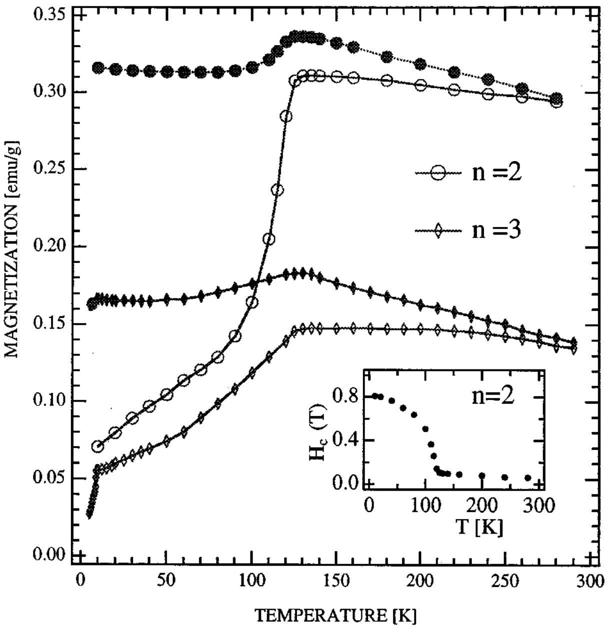

FIG. 1. Magnetization vs temperature curves ($H=0.1\,\mathrm{T}$) for FePc-intercalated BISCO $n=3$ (diamonds) and $n=2$ (circles) samples. Open and closed symbols refer to ZFC and FC values of magnetization, respectively. The inset shows sharp increase of the coercive field, H_c below 130 K in the $n=2$ sample.

It is interesting to note that the transition temperature was only weakly sensitive to H: T_0 shifted from ~ 130 down to $\sim 125\,\mathrm{K}$ when H was increased from 10^{-3} to 1 T. Also, T_0 was virtually the same for the FePc-intercalated $n=2$, $n=3$ (Fig. 1), and $n=4$ samples, as well as in the $n=2$ and $n=3$ samples intercalated with mixed MPc (such as $\mathrm{Ni_{1/3}Fe_{2/3}Pc}$, $\mathrm{Cu_{1/2}Fe_{1/2}Pc}$, or $\mathrm{Pb_{1/4}Fe_{3/4}Pc}$). However, the transition could not be observed in either of the purely NiPc-, PbPc-, or CuPc-intercalated (that is, not containing any significant amount of FePc) samples.

B. Electrical resistivity

In contrast to the magnetism, the dc resistivity appeared to be very much dependent on the host system (Figs. 2 and 3). For the $n=3$ and $n=4$ hosts, ρ decreased with cooling in a nearly linear fashion, similar to the normal-state ρ vs T curves of the nonintercalated superconducting high-T_c oxides (Fig. 3). The specific type of intercalated MPc had very little if any effect on the ρ vs T curves of the $n=3$ and 4 samples. However, for the $n=2$ system, ρ generally had a tendency to increase with cooling, and the ρ vs T curves exhibited a complicated shape depending on the type of intercalated MPc. In particular, ρ in the FePc intercalate was slightly decreasing upon cooling from 300 down to 200 K, as well as below 40 K, in contrast to the monotonously increasing ρ in the NiPc intercalate (Fig. 2).

Finally, it is interesting to note that both the dc magnetization and resistance curves revealed a superconducting transition in both the FePc- and the NiPc-intercalated $n=3$ samples. The onset transition temperature was $\sim 9.5\,\mathrm{K}$ and the ρ vs T curves, in general, were also almost identical for both samples, indicating that the particular metal in intercalated MPc had little effect on resistivity. Similarly, the ρ vs T curves did not exhibit notable differences in FePc- and NiPc-intercalated $n=4$ samples, in contrast to the $n=2$ sys-

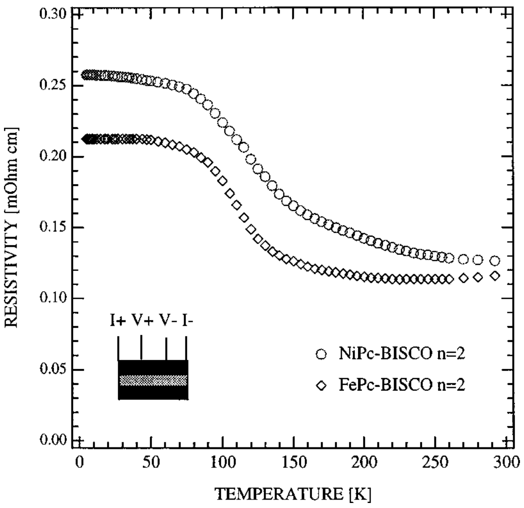

FIG. 2. Resistivity vs temperature curves for the NiPc- (circles) and the FePc-intercalated (diamonds) $n=2$ samples. The inset shows four equally spaced electrical probes attached linearly to the surface of the pellet. The filled and the shaded areas represent the conducting $x=0.10$ and the insulating $x=0.05$ phases, respectively.

tem. However, only the $n=3$ samples have been found so far to exhibit superconductivity. The fact of the coexistence of superconductivity with a relatively large MR in the FePc-intercalated $n=3$ system is intriguing, even though at this stage these two phenomena do not seem to be related.

C. Magnetoresistance

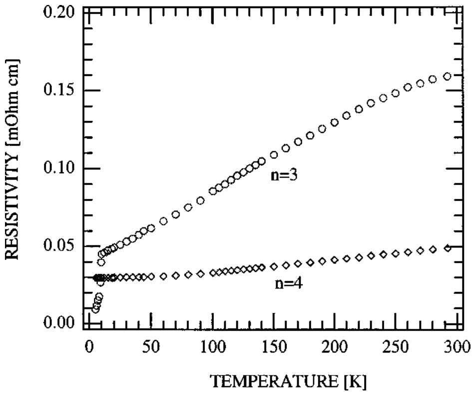

FIG. 3. Resistivity vs temperature curves for the FePc-intercalated $n=3$ (circles) and $n=4$ (diamonds) samples.

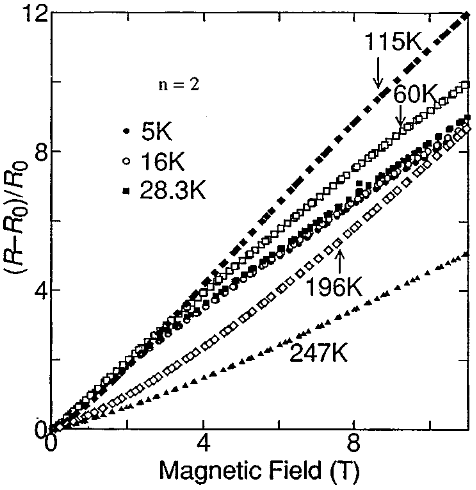

FIG. 4. MR vs applied field in the FePc-intercalated $n=2$ sample.

Very large positive values of MR>1200% were obtained at ~130 K in the FePc-intercalated BISCO $n=2$ samples (Fig. 4). These MR values exceed those obtained typically in GMR multilayer films[8–10] and are comparable to the CMR values observed in Mn oxides.[11–14] In terms of a crystal structure, our system is also different from multilayers, but close to Mn oxides. It should be noted, however, that in both above systems MR is usually negative; that is, resistance is *decreasing* with applied field, in contrast to our samples, where R is *increasing* with applied field. The MR vs T curves exhibit a distinct maximum around the magnetic transition temperature, $T_0 \sim 130$ K (Fig. 5). This is a strong indication that the anomalous large MR exhibited by our samples may be related to the magnetic transition. Similarly, in the case of Mn oxides, the CMR was observed to peak near the ferromagnetic to paramagnetic transition temperature.[11–14]

The magnitude of MR was found to be very sensitive to the host oxide: in particular, it dropped to ~40% in the FePc-intercalated $n=3$ and ~0% $n=4$ samples. We have also found that the values of MR decreased significantly if FePc (as an intercalant) was replaced, either partially or completely, with other MPc, such as NiPc, CuPc, H_2Pc, or PbPc. In particular, the MR values for the $n=2$ system dropped down to 850% and 300% in the cases of mixed-metal $Ni_{1/3}Fe_{2/3}$Pc (prepared by a cosublimation of one part NiPc and two parts FePc; see Fig. 5) and pure NiPc, respectively. This result correlates with the decreased saturation magnetization values, measured at 10 K, in the NiPc-containing samples (~0.30 and ~0.03 emu/g, respectively). The MR (as well as the saturation magnetization) values dropped virtually down to zero in the cases if either CuPc, H_2Pc, or PbPc were used as an intercalant, independent of the host oxide.

D. Discussion

The physical mechanism responsible for the observed anomalous large MR in the intercalated Cu oxides is not clear at present. At this stage, one can speculate that MR

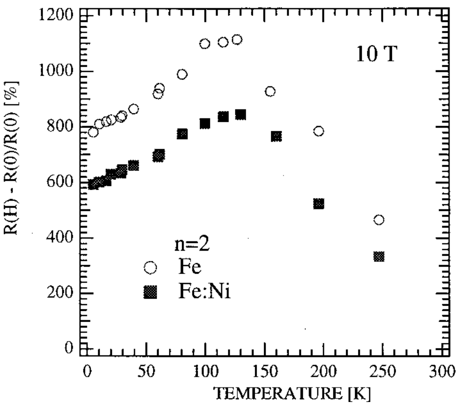

FIG. 5. Temperature dependence of MR (%) at 10 T in the FePc- and the mixed-metal $Ni_{1/3}Fe_{2/3}$Pc-intercalated $n=2$ samples.

depends on interactions between the transition metal $3d$ orbitals of the intercalated MPc molecules and conduction electrons of the host oxide. These interactions will be determined by important material-related factors. The first factor is electronic configuration of $3d$ orbitals, in particular, availability of unpaired electrons in the orbitals with z component, $3d_{z^2}$, $3d_{xz}$, and $3d_{yz}$, which can be expected to interact with the adjacent Bi-O layers of the host oxide (e.g., oxygen $2p_z$ orbitals). The Ni^{2+} ions in the NiPc-intercalated $n=2$ system were shown to be in a high-spin, $s=1$ state with two unpaired spins occupying $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals,[4] while in the case of CuPc, there is only one unpaired spin, $s=1/2$, and it is located in $3d_{x^2-y^2}$ orbital with no density along z direction. A more favorable configuration is achieved in the case of FePc, where Fe^{2+} ions are in intermediate spin state $(s=1)$ with unpaired spins in two important orbitals: $3d_z2$ and twofold degenerate $3d_{xz,yz}$. Ferromagnetic ordering of Fe^{2+} ions intercalated into $n=2$ host would give rise to a saturation magnetization moment of $\sim$0.45 emu/g, close to the experimentally observed value ($\sim$0.5 emu/g).

Another important factor is the number of electrically conducting (Cu-O) layers in the host oxide. In the case of $n=2$ host, both Cu-O layers in the unit cell block are ''external'' and can be directly influenced by changes in Bi-O layers which are considered to be a charge reservoir. However, in the $n=3$ and $n=4$ hosts, there are respectively one and two ''interior'' Cu-O layers which are screened from Bi-O layers by the ''external'' Cu-O layers. The charge balance in these ''interior'' Cu-O layers is less sensitive to intercalation and attendant changes in the Bi-O layers adjacent to intercalated MPc molecules. Hence ρ vs T curves can be strongly influenced by intercalation in $n=2$ host, while in $n=3$ and 4 hosts metallic character is retained. Also, MR values were observed to drop dramatically with increasing n, that is, increasing ratio of ''interior'' to ''external'' Cu-O layers, indicating that it is the charge transport in ''external'' Cu-O layers that is most sensitive to the applied magnetic field. From this point of view, $n=1$ host seems interesting as the single Cu-O layer will be exposed to influences from both sides.

To further explore and optimize MR in the intercalated Cu-oxide system, other potentially promising host materials, such as BISCO $n=1$, or magnetic metal (such as Ni, Co, or Mn)-based oxides, could be intercalated with MPc. Another dimension worthy to be explored is the central metal in MPc. So far, the FePc proved to be the best choice, but other candidates such as Mn, Co, $4d$ and $5d$ transition metal MPc and their combinations may be interesting.

In summary, an anomalous large MR of over 1200% has been observed in the intercalated Cu oxides. We relate the possible mechanism responsible for the observed MR to a magnetic transition at ~ 130 K, and believe that this work may open an avenue to creating large MR materials.

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