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A novel hybrid of high-T_c cuprate and paramagnetic organic radical

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Abstract

We have found a heterostructured spin-system consisting of superconducting and paramagnetic sub-systems, where free radicals ($S = 1/2$) are stabilized between Bi-based cuprate layers. The superconducting-paramagnetic dual magnetism observed in this work may provide a useful probe for investigating the mechanism of high transition temperature (high-T_c) superconductivity. The stabilization of solid-state free radicals in-between (super) conductive layers is expected to provide a new class of magnetic heterostructures with unusual functionalities, which may find applications as magneto-electronic materials or devices.

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1. Introduction

The most challenging question on high-T_c superconductivity is what interaction makes the transition temperature (T_c) high and mediates the electron pairing. In the cuprate superconductors, the static antiferromagnetic order in the CuO_2 plane usually disappears and is replaced by strong antiferromagnetic fluctuations upon hole doping, leading to superconducting transition. In this respect, it has been suggested that two-dimensional (2D) spin structure interrelated with the charge carrier density within the CuO_2 plane is of crucial importance for the superconducting transition as well as for the T_c regulation. Intercalation chemistry applied to high-T_c cuprate superconductors have provided a way of controlling the dimensionality as well as modifying the charge carrier density in the superconductively active CuO_2 layer [1–7]. There have been reported that inorganic species can be intercalated into Bi-based high-T_c cuprates [1–4]. However, the incorporation of organic moiety [5–7] into the layered cuprate has tremendous advantages over inorganic species [1–4] for studying high-T_c superconductivity as well as for creating new materials with unusual features, since organic compounds show the widest variety of geometric and chemical nature ranging from neutral molecules to various ions, even to free radicals. Although the evolution of T_c in these intercalation compounds has been mainly attributed to a change in the electronic structure of CuO_2 plane, the micro-mechanism of T_c enhancement or suppression is still an open question. The hybrid material, if only the free radical with unpaired electronic spin ($S = 1/2$) can be hybridized with the layered high-T_c cuprate, will contribute to solve the hotly debated issue on the superconductivity, because a free radical behaves as localized spin, i.e. magnetic pair-breaker. Based on this this methodology, it will also helpful to develop nanostructures in which the conducting and paramagnetic subsystems interact cooperatively to exhibit unusual physical properties.

The initial motivation of this study was to obtain relationship between the superconductivity and the 2D magnetic couplings involving 3d-transition metal ions (Cu^{2+}/Cu^{3+}) which most possibly play an essential role in the mechanism of superconductivity, and, therefore, we focused on the evolution of electronic spin interaction in a series of intercalated $Bi_2Sr_2CaCu_2O_y$ (Bi2212) by

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measuring electron paramagnetic resonance (EPR) spectroscopy. In this process, we have unexpectedly found out a new type of heterostructured spin-system with discrete superconducting and paramagnetic layers.

2. Experiment

The pristine Bi2212 was synthesized by conventional solid state reaction with nominal composition of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_y$. In an effort to avoid oxygen defect sites in the CuO_2 plane and consequently to guarantee uniform spin-structure, the as-prepared compound was annealed at 500 °C in air for 72 h [8,9]. The HgI_2–intercalated Bi2212 (HgI_2–Bi2212) was prepared by heating the HgI_2 and the pristine in a vacuum-sealed Pyrex tube, as reported previously [3]. Then two types of organic intercalation compounds were prepared. One is $(PyMe)_2HgI_4$ (Py = pyridine; Me = $-CH_3$) intercalated Bi2212 [5], which was prepared by solid state reaction between the HgI_2–Bi2212 and methylpyridinium iodide (PyMeI) at 100 °C for 12 h. The other is $(Me_3S)_2HgI_4$ intercalated one [6], which was synthesized by solvent-mediated reaction between the HgI_2–Bi2212 and trimethylsulfonium iodide (Me_3SI) at 70 °C for 12 h with acetonitrile as the mediating solvent. The chemical formulae of the organic intercalates were determined to be $[(PyMe)_2HgI_4]_{0.35}Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_y$ [$(PyMe)_2HgI_4$–Bi2212] and $[(Me_3S)_2HgI_4]_{0.34}Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_y$ [$(Me_3S)_2HgI_4$–Bi2212]. From the powder X-ray diffraction analyses, it is revealed that basal spacing is increased by 10.8 and 12.6 Å upon $(PyMe)_2HgI_4$- and $(Me_3S)_2HgI_4$-intercalation, respectively, compared to the pristine Bi2212 [5,6]. The characteristics of electronic spin interaction in each compounds has been investigated by EPR spectroscopy at room temperature. The magnetic properties of the samples have been measured in weak- ($H = 20$ G) and high-magnetic field ($H = 2$ T), using superconducting quantum interference device (SQUID) magnetometer.

3. Results

Fig. 1 shows the EPR spectra for the Bi2212 and its organic salt-intercalates. The asymmetric EPR spectral features of copper ion indicate a superposition of two anisotropic components, one sharp signal and a broad anisotropic one. For the $(PyMe)_2HgI_4$- and $(Me_3S)_2HgI_4$-intercalates, the intensity of Cu 3d EPR signal is significantly enhanced, at least by an order of magnitude compared to the pristine Bi2212, even though there have been several reports that superconducting cuprates are EPR silent [10,11]. This drastic increase in Cu 3d EPR intensity may be explicable in terms of electronic exchange interactions between the paramagnetic centres (Cu^{2+}) in the d-transition metal compounds [12–14]. In this scheme known as exchange narrowing, the EPR spectra are characterized by a sharp EPR line, where strong electronic exchange in a lattice causes rapid motion of an individual spin throughout the crystalline array, in this case the CuO_2 layer. This then has the effect of averaging the interactions, which would normally have a broadening effect, leading to a sharp signal. Taking into account electronic charge transfer from the HgI_4^{2-} to the host lattice upon organic-salt intercalation [5,6], it is reasonably expected that subtle changes in the geometric and electronic structures of copper reinforce the electronic exchange within the CuO_2 plane and as a result 2D dynamic spin-structure is substantially modified [15].

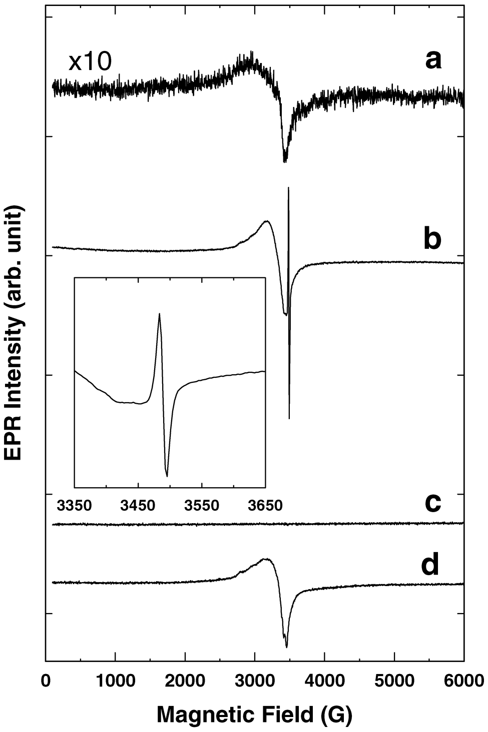

Fig. 1. X-band EPR spectra for (a) the Bi2212, (b) the $(Me_3S)_2HgI_4$–Bi2212, (c) the free $(Me_3S)_2HgI_4$, and (d) the $(PyMe)_2HgI_4$–Bi2212. The inset represents the enlarged EPR spectral line of $(Me_3S)_2HgI_4$-intercalate at around 3500 G. All the EPR measurements were carried out at room temperature.

Although both type of organic salt-intercalates show similar Cu 3d EPR spectra, the $(Me_3S)_2HgI_4$-intercalate exhibits a sharp resonant EPR peak centred at 3489 G (Fig. 1(b)), distinguished from the $(PyMe)_2HgI_4$-intercalate (Fig. 1(d)). The peak-to-peak line width (ΔH_{pp}) was determined to be 12 G and the g-factor was calculated to be $g = 2.002$, which corresponds to the characteristic value for a free unpaired electron ($S = 1/2$), that is, free radical. This result indicates that the trimethylsulfonium cation (Me_3S^+) is the origin of the free radical, because the only difference for the two organic salt-intercalates is the organic cation incorporated in the form of complex salts, $(PyMe)_2HgI_4$ and

$(Me_3S)_2HgI_4$. The EPR spectrum of the free $(Me_3S)_2HgI_4$ salt represents no sign of free radical (Fig. 1(c)). It is, therefore, concluded that the sharp resonant EPR peak of the $(Me_3S)_2HgI_4$–Bi2212 should result from the sulfonium cation Me_3S^+ under exotic chemical environment of interlayer space. This implies that there occurs an intermolecular charge-transfer [16] from the HgI_4^{2-} to the Me_3S^+ as well as a charge-transfer from the HgI_4^{2-} to the cuprate lattice [5,6], forming a meta-stable species of $[Me_3S\cdot]^0$ and $HgI_4^{(2-\delta)-}$ in-between the cuprate blocks.

Fig. 2 shows the structural model of the $(Me_3S)_2HgI_4$-intercalate, where we can anticipate that the 2D array of paramagnetic spins may be converted into spin-aligned state by applying magnetic field. In this respect, the existence of free radical was also confirmed by measuring temperature dependent magnetization at high magnetic field $H = 2$ T.

Fig. 3(a) and (b) shows the temperature dependent magnetizations (M) for the $(Me_3S)_2HgI_4$–Bi2212 (spin-active) and $(PyMe)_2HgI_4$–Bi2212 (spin-inactive), respectively. The $(Me_3S)_2HgI_4$-intercalate shows the paramagnetic behavior from 300 down to 80 K (Fig. 3(a)), where the magnetization (M) increases towards lower temperature due to the alignment of the free electronic spins. Thereafter, the magnetization declines down to a minimum at 30 K owing to the superconducting transition at 80 K, and then rises again. In Fig. 3(a), the pit at around 30 K is an effect of interplay between diamagnetic shielding contribution of the superconducting host and the paramagnetic contribution of the guest. This superconducting-paramagnetic dual magnetism strongly suggests that the superconductivity is 2D and confined to the metallic layers. Here, interlayer coupling of the order parameter by Josephson tunneling seems to be unlikely, since the free radical spins in the interlayer space may act as scavengers for the Cooper-pair tunneling. Different from the $(Me_3S)_2HgI_4$–Bi2212, $(PyMe)_2HgI_4$-intercalate shows only typical superconducting transition at 80 K (Fig. 3(b)), indicative of the absence of spin-active paramagnetism. As can be seen in Fig. 3, both the $(Me_3S)_2HgI_4$- and the $(PyMe)_2HgI_4$-intercalates exhibit magnetic transition at around 20 K, which may be understood by the thermodynamic phase transition of magnetic flux-line (vortex) in the highly anisotropic type-II superconductors [17–21].

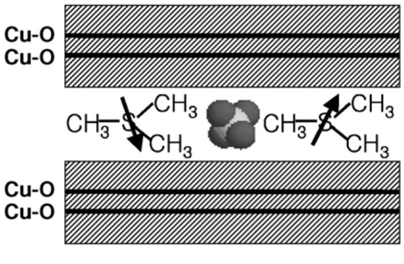

Fig. 2. Schematic illustration of the $(Me_3S)_2HgI_4$–Bi2212, where the tetrahedral unit and the arrow indicate the HgI_4^{2-} and the unpaired electronic spin, respectively.

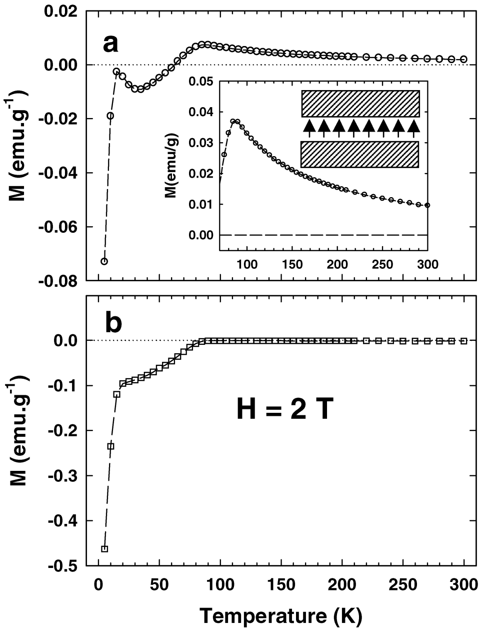

Fig. 3. Temperature dependence of zero-field-cooled magnetization (M) for (a) the $(Me_3S)_2HgI_4$–Bi2212 and (b) the $(PyMe)_2HgI_4$–Bi2212 in an applied magnetic field of 2 T. The dashed-line is a guide to the eye. The inset in (a) represents the enlarged view of paramagnetic behavior and the schematic illustration of spin-alignment in the intercalant layer.

While the combined analysis of EPR measurement and high-field magnetization suggests a paramagnetism due to the intercalation-induced free radical spins, more reliable information is found in the $\chi T - T$ plot. Fig. 4(a) and (b) shows the temperature dependent χTs (product of susceptibility and temperature) for the $(Me_3S)_2HgI_4$- and $(PyMe)_2HgI_4$–Bi2212, respectively. Although the $(Me_3S)_2HgI_4$-intercalate and the $(PyMe)_2HgI_4$-one represent different behaviors in the temperature dependent magnetization (M) under high magnetic field $H = 2$ T (Fig. 3(a) and (b)), a parallel behavior is observed in the χT for both types of intercalates (Fig. 4(a) and (b)). Here, it is worth noting that the $\chi T - T$ plot for the $(Me_3S)_2HgI_4$-intercalate appears to be shifted upward compared to the $(PyMe)_2HgI_4$-one. This upward shift of $\chi T - T$ plot is predominantly attributed to the *isolated* free radical spins in the $(Me_3S)_2HgI_4$–Bi2212, causing Curie-type paramagnetic contribution. In Fig. 4(a) and (b), both $(Me_3S)_2HgI_4$- and $(PyMe)_2HgI_4$-intercalates show slightly increasing χTs with decreasing temperature in the range 300–80 K, indicative of weak ferromagnetism. This weak ferromagnetism is attributed to the local ferromagnetic coupling between oxygen holes and adjacent Cu^{2+} (d^9) electrons in the hole-doped CuO_2 plane [22]. As mentioned above, a comparative inspection of $\chi T - T$ plots for the $(Me_3S)_2HgI_4$- and $(PyMe)_2HgI_4$-intercalates reveals that the spin-active guest (free radical) gives the Curie-paramagnetism, which can also disentangle the magnetic

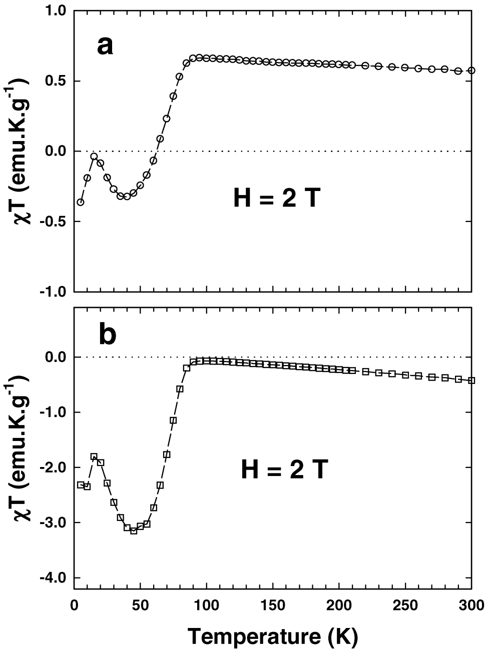

Fig. 4. χTs as a function of temperature for the (a) the $(Me_3S)_2$-HgI_4–Bi2212 and (b) the $(PyMe)_2HgI_4$–Bi2212, respectively, which were derived from zero-field-cooled magnetizations (M) in an applied magnetic field of 2 T.

effects of the superconducting host and of the localized free radical spins in the intercalant.

Fig. 5 shows the temperature dependent d.c. magnetizations for the pristine Bi2212 and its intercalates measured in a weak magnetic field of 20 G. For all the samples, there cannot be seen any sign of magnetic transition near at 20 K that would be, if any, indicative of secondary superconducting material. It is, therefore, strongly suggested that superconductivity and paramagnetism can coexist in a molecule-level layer-by-layer system. The nearly invariant onset T_c upon HgI_2-intercalation (HgI_2–Bi2212; $T_c \approx 78$ K) is attributed to the air-annealed pristine Bi2212 ($T_c \approx 78$ K) in this work. The $(Me_3S)_2HgI_4$- and the $(PyMe)_2HgI_4$-intercalates shows onset T_c of 80 K, comparable to those of the high-field magnetic property measurements.

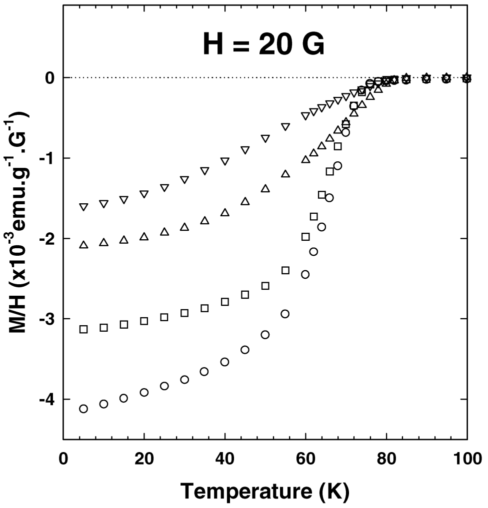

Fig. 5. Zero-field-cooled (ZFC) d.c. magnetizations of the pristine Bi2212 and its intercalatates measured with a superconducting quantum interference device (SQUID) magnetometer in a magnetic field of 20 G. Data points represent the Bi2212 (○), the HgI_2–Bi2212 (□), and the $(PyMe)_2HgI_4$–Bi2212 (△) and the $(Me_3S)_2$-HgI_4–Bi2212 (▽).

4. Conclusion

In summary, we have chemically created the heterostructured magnetic system that combines high-T_c cuprate and paramagnetic free radical, which is confirmed microscopically through EPR measurement and macroscopically through temperature dependent magnetization. The superconducting-paramagnetic dual magnetism and the prominent Cu 3d EPR signal in this system, indicate that the superconductivity is closely related to the 2D spin interaction within the CuO_2 plane and the coupling between layers is not important for the stability of the superconducting state. The unprecedented hybrid of Bi-based cuprate and free radical has electronically (host) and magnetically (guest) active parts, whose cooperation would possibly make the magneto-transport a very novel one. In this respect, the ability of incorporating free radical spins into the metallic layers would be highly desirable from fundamental and technological aspects, particularly in the viewpoint of recently developing fields, magneto-electronics or spintronics [23–27]. It would be interesting and challenging work to investigate tunneling magnetoresistance (TMR) [28] for the chemically prepared magnetic heterostructures, since spin- or magnetic field-dependent interlayer tunneling effect might be induced due to the possible control of spin degree of freedom in the intervening barrier layers by applying magnetic field.

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References

[1] X.D. Xiang, S. Mckernan, W.A. Vareka, A. Zettl, J.L. Corkill, T.W. Barbee III, M.L. Cohen, Nature 348 (1990) 145.

[2] G. Liang, A. Sahiner, M. Croft, W. Xu, X.D. Xiang, D. Badresingh, W. Li, J. Chen, J. Peng, A. Zettl, F. Lu, Phys. Rev. B 47 (1993) 1029.

[3] J.H. Choy, N.G. Park, S.J. Hwang, D.H. Kim, N.H. Hur, J. Am. Chem. Soc. 116 (1994) 11564.

[4] J.H. Choy, S.J. Hwang, N.G. Park, J. Am. Chem. Soc. 119 (1997) 1624.

[5] J.H. Choy, S.J. Kwon, K.S. Park, Science 280 (1998) 1589.

[6] S.J. Kwon, J.H. Choy, D. Jung, V. Huong, Phys. Rev. B 66 (2002) 224510.

[7] S.J. Kwon, J.H. Choy, Inorg. Chem. 42 (2004) 8134.

[8] T. Ishida, K. Koga, S. Nakamura, Y. Iye, K. Kanoda, S. Okui, T. Takahashi, T. Oashi, K. Kumagai, Physica C 176 (1991) 24.

[9] R.J. Singh, P.K. Sharma, A. Singh, S. Khan, Physica C 356 (2001) 285.

[10] F. Mehran, P.W. Anderson, Solid State Commun. 71 (1989) 29.

[11] P. Simon, J.M. Bassat, S.B. Oseroff, Z. Fisk, S.W. Cheong, A. Wattiaux, S. Schultz, Phys. Rev. B 48 (1993) 4216.

[12] C.J. Gorter, J.H. Van Vleck, Phys. Rev. 72 (1947) 1128.

[13] J.H. Van Vleck, Phys. Rev. 74 (1948) 1168.

[14] P.W. Anderson, P.R. Weiss, Rev. Mod. Phys. 25 (1953) 269.

[15] B.I. Kochelaev, J. Sichelschmidt, B. Elschner, W. Lemor, A. Loidl, Phys. Rev. Lett. 79 (1997) 4274.

[16] A.J. Macfalane, R.J.P. Williams, J. Chem. Soc. (A) (1969) 1517.

[17] L.L. Daemen, L.N. Bulaevskii, M.P. Maley, J.Y. Coulter, Phys. Rev. Lett. 70 (1993) 1167.

[18] R. Sásik, D. Stroud, Phys. Rev. Lett. 72 (1994) 2462.

[19] D.R. Nelson, Nature 375 (1995) 356.

[20] E. Zeldov, et al., Nature 375 (1995) 373.

[21] A. Grigorenko, S. Bending, T. Tamegai, S. Ooi, M. Henini, Nature 414 (2001) 728.

[22] G. Chen, W.A. Goddard III, Science 239 (1988) 899.

[23] G.A. Prinz, Science 282 (1998) 1660.

[24] E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, V. Laukhin, Nature 408 (2000) 447.

[25] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, K. Ohtani, Nature 408 (2000) 944.

[26] S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnár, M.L. Roukes, A.Y. Chtchelkanova, D.M. Treger, Science 294 (2001) 1488.

[27] S.D. Ganichev, E.L. Ivchenko, V.V. Bel'kov, S.A. Tarasenko, M. Sollinger, D. Weiss, W. Wegscheider, W. Prettl, Nature 417 (2002) 153.

[28] J.S. Moodera, R. Meservey, X. Hao, Phys. Rev. Lett. 70 (1993) 853.