Surface Review and Letters, Vol. 9, No. 2 (2002) 1109–1112

COEXISTENCE OF FERROMAGNETISM AND HIGH-TEMPERATURE SUPERCONDUCTIVITY IN Dy-DOPED BiPbSrCaCuO

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Ferromagnetism was found to coexist with superconductivity in Dy-doped BiPbSrCaCuO-2212 single crystals up to the superconducting critical temperature $T_c \sim 80$ K. Several experimental tests indicated that the phenomenon is intrinsic to the entire specimen rather than due to separate phases or to isolated impurities.

The interplay of ferromagnetism and superconductivity is obviously a topic of great fundamental and practical interest. Specifically, weak ferromagnetism was recently reported to coexist with superconductivity in heavy-fermion specimens.[1–3] Even more recently, the discovery[4] that ferromagnetism exists together with superconductivity in high-temperature superconductors (HTSC) of the EuCeRuSrCuO family stimulated extreme interest.

We report the coexistence of the two phenomena in a different HTSC family: Dy-doped $Bi_{2-x}Pb_xSr_2Ca_{1-y}Dy_yCu_2O_{8+\delta}$. Single crystal samples which clearly exhibit such coexistence below the superconducting critical temperature $T_c \sim 80$ K, whereas ferromagnetism persists at least up to room temperature.

The novelty and importance of the result stem not only from the intrinsic interest of the coexistence of possibly antagonistic phenomena, but also from the fact that most of the previous perovskite magnetic superconductors contain Ru. Ferromagnetism in this family of superconductors is believed to originate from the RuO sublattice, similar in structure to ferromagnetic $SrRuO_3$.[4,5] In our samples, since there is no Ru, other mechanisms for the coexistence ferromagnetism at the rather high superconducting critical temperature would have to be reconsidered.

Large-size $Bi_{2-x}Pb_xSr_2Ca_{1-y}Dy_yCu_2O_{8+\delta}$ single crystals with y ranging from 0 to 1 were grown by a nonstoichiometric self-flux method. The starting oxides, carbonates and nitrates were prereacted and then melted at 1100°C. The melt was cooled at a rate of 3°C/h to 940°C, then at 1°C/h to 800°C and finally at 50°C/h to 20°C in air. Platelike crystals with facets of size up to $5 \times 5 \times 0.05$–0.5 mm^3 were then extracted from the crucible. In this work, only the result from the sample with Dy ≈ 0.05 is presented.

X-ray diffraction measurements were performed with both conventional tube source and synchrotron X-rays from the 5C2 beamline of the Pohang Light source, Pohang, Korea. X-ray absorption spectroscopy of the Dy, O and Cu edges was performed at the HSGM beamline of SRRC (Synchrotron Radiation Research Center, Taiwan).

The existence of ferromagnetism together with superconductivity is indicated, first of all, by magnetic susceptibility data, taken with a Quantum Design SQUID magnetometer, like those of Fig. 1. The top part [Fig. 1(a)] shows the ferromagnetic hysteresis loop at 300 K. The coercive field was found to increase with decreasing temperature, as expected for ferromagnetic specimens.[6] Figure 1(b) shows the superconducting response at 10 K. Figure 1(c) shows the transition from a purely ferromagnetic behavior (80 K) to a superimposed ferromagnetic and superconductive behavior (75 K).

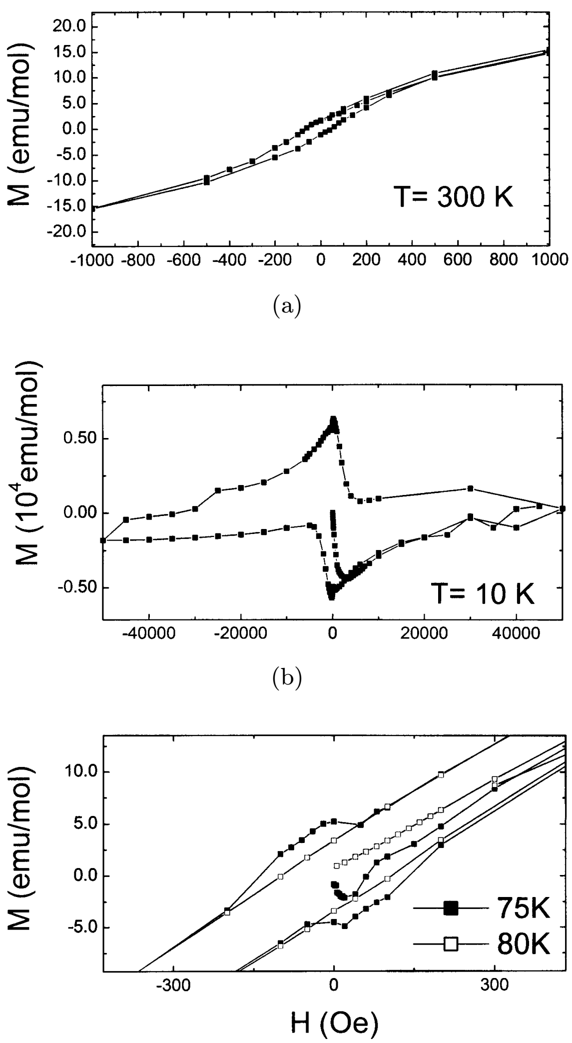

Fig. 1. Magnetic moment versus the magnitude of the H-field for (a) 300 K, (b) 10 K and (c) 75 and 80 K.

Figure 2 shows direct evidence of superconductivity from resistivity measurements as a function of temperature (top) and from zero-field-cooled magnetic moment data versus temperature. The data of Fig. 2(b) are for the crystal plane (*ab*) and for the perpendicular (*c*) direction. As expected for Meissner effect in a superconductor,

$$\frac{M}{V} = -\frac{1}{4\pi}\frac{H}{(1-N)},$$

where M is the measured moment, V the sample volume, N the demagnetization factor, and H the external field. When the external field H is applied in the *ab* plane, the demagnetization factor N is close

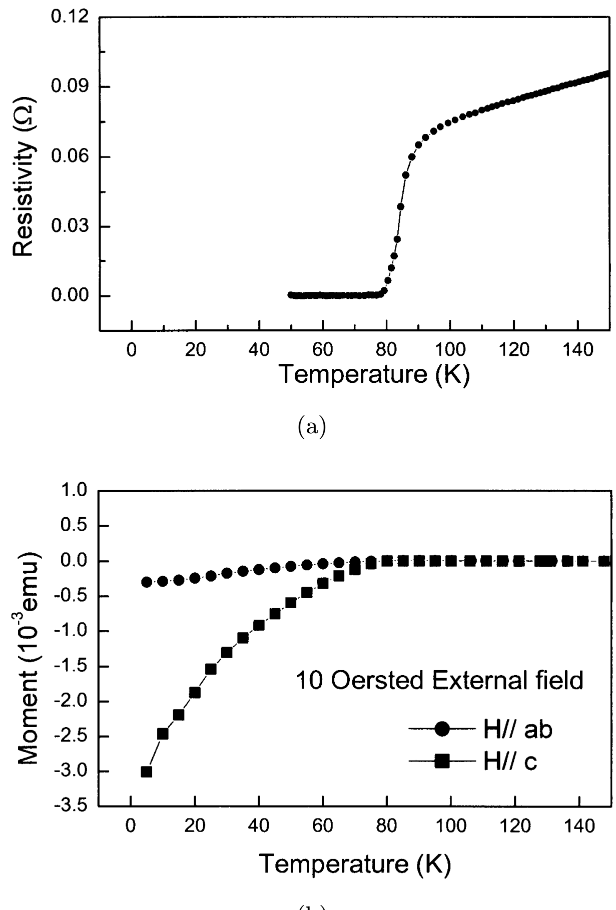

Fig. 2. (a) Resistivity vs. temperature showing a superconducting transition at ≈ 80 K. (b) Zero-field magnetic moment vs. temperature. The full dots are for the *ab* plane and the squares are for the *c*-direction. The mass of the sample is 1.2 mg.

to zero and we have a complete shield of the magnetic flux at low temperature. When H is applied along the c axis, the measured moment is 10 times larger due to the demagnetization factor. This is in agreement with our sample geometry.

The superconducting transition temperature range measured by magnetic moment is much wider than by resistivity. This indicates that magnetic flux can penetrate into our sample at a temperature much lower than T_c, despite the high quality of our single-crystal samples.

The crucial issue, of course, is to rule out the possibility that superconductivity and ferromagnetism belong to two different phases, or that ferromagnetism is due to isolated Dy microparticles. Extensive characterization with high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), electron probe microanalysis (EPMA) X-ray absorption spectroscopy (XAS) and infrared (IR) spectroscopy provides good evidence against these hypotheses.

First of all, Dy microparticles cannot explain room-temperature ferromagnetism: the Curie temperature for bulk Dy is $\sim$ 90 K, and does not show substantial increase for Dy nanoparticles.[7] We also studied the effects of oxygen depletion from our samples: the samples became nonsuperconducting, enabling us to measure the ferromagnetic signal at low temperatures. The measured M vs. H/T curves are not consistent with the superparamagnetic behavior of isolated small particles.[7]

Could our room-temperature ferromagnetic signal originate from impurities other than Dy? Suitable candidates could be Fe, Ni or Co. However, XAS and EPMA tests ruled out the presence of enough impurities of this kind to justify the strength of our ferromagnetic signal.

XRD measurements revealed high-quality single-crystal characteristics with no evidence of mixed phases. Sharp X-ray diffraction peaks show in fact that the average crystal coherence is of the order of 0.2 μm. XRD data, as shown in Fig. 3, also revealed lattice parameters different from undoped $Bi_{2-x}Pb_xSr_2Ca_{1-y}Dy_yCu_2O_{8+\delta}$ — specifically, a $\sim$ 0.4% c-axis contraction is detected compared to BiSrCaCuO single crystals, whereas the Pb doping induced a c-axis expansion of $\sim$ 0.36%. XRD data of samples of different composition are also shown in Fig. 3. The clear trend of the displacement of the diffraction peaks indicates that the Dy doping does indeed affect the crystal lattice. Internal displacements of CuO2 and SrO planes are also detected.[8] This indicates that Dy is not in a separate phase but contributes as a dopant to the overall properties of the entire crystal.

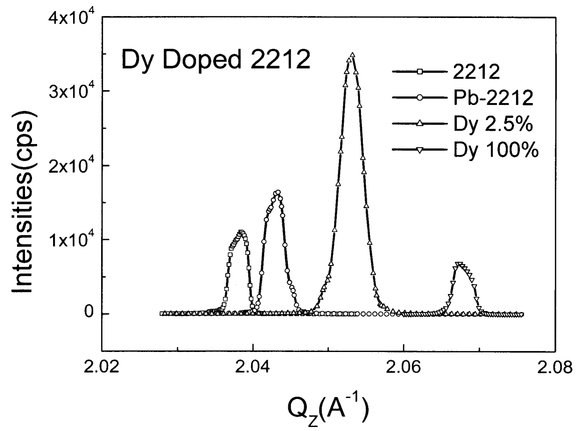

Fig. 3. Synchrotron XRD measurement of the Dy-doped 2212 samples with different Dy concentration. Data of pure 2212 and Pb-doped 2212 samples are also shown for comparison. The clear shift of the Bragg peak position indicates the effect of Dy doping on the lattice spacing.

The XRD and HRTEM data also revealed an in-plane $\sim$ 20-unit-cell superstructure modulation along (110), whereas Pb-free undoped specimens exhibit an incommensurate 5×1 modulation along (010) — and undoped Pb-containing specimens show no superstructure at all.[9] This again indicates that Dy acts as a dopant in the entire crystal rather being in a separate phase.

IR reflectance data showed no strong phonon features, providing further evidence against a phase separation. Specifically, for a phase separation with superconducting/metallic and magnetic/insulating regions, one would expect optical phonon features from the insulating phase. This argument would not apply to the specific case of a metallic magnetic region with nearly the same electron density as the superconductor. However, this specific result is consistent with the overall picture of the other experiments, speaking against a phase separation.

We thus conclude that the coexistence of superconductivity and magnetism in this family of materials is not a spurious effect but an intrinsic property. Our material is ferromagnetic at room temperature and becomes superconducting at ∼ 80 K while remaining ferromagnetic. These properties have an obvious impact not only on superconductor technology but also on the fundamental issues concerning the nature of high temperature superconductivity.

Acknowledgments

This work was supported by the Fonds National Suisse, the Ecole Polytechnique Fédérale de Lausanne, the U.S. National Science Foundation through grant DMR-9705108, and the National Science Council of Taiwan.

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