Search for Circular Dichroism in High-T_c Superconductors

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We report observation of circular dichroism in reflection from various cuprate superconducting materials, including $YBa_2Cu_3O_{7-x}$ films, an etched $YBa_2Cu_3O_7$ crystal, and a $Bi_2Sr_2CaCu_2O_8$ crystal. This signal develops as T is lowered below 200 K and exhibits little change near T_c. The exact onset temperatures differ for the various materials.

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Since the discovery of the high-temperature oxide superconductors,[1] many proposals have surfaced[2] for the mechanisms responsible at a microscopic level. One of the more unusual classes of such proposals stems from a suggestion by Laughlin,[3] based upon an analogy with fractional quantum Hall systems. This model predicts the breakdown of time-reversal symmetry at or above the superconducting transition temperature T_c. Since that original proposal, a number of more detailed treatments of "anyon superconductivity" have appeared.[4] The breakdown of time-reversal symmetry appears as a consequence of the two-dimensional (2D) nature of the conduction planes, and is expected to occur as a well-defined phase transition at a temperature $T_{tp} \geq T_c$, where time-reversal and parity symmetries are broken simultaneously. This suggestion is made more startling by the apparent paradox posed by the Meissner effect of a superconductor and the internal field predicted by the anyon models. If such a broken symmetry occurs, then a circular dichroism (CD) should be present below T_{tp} in the superconducting oxides.[5] In the present work we report on experimental observations of CD in superconducting cuprate materials. We find a signature of CD which appears on cooling well above T_c and is virtually unaffected on traversing T_c itself. The signal disappears in a film annealed into the insulating state.

There appear to be no truly reliable estimates of the anticipated size of the CD signal. Certainly, the intrinsic value of the CD might be quite small and, moreover, we would expect that our laser spot would average over several independent regions, reducing the observed magnitude still further. The presence of linear birefringence (γ) in the optical components and in the sample causes an interfering signal which must be rejected. We have developed a new technique which improves our rejection of γ by 2–3 orders of magnitude. Namely, we rotate the incident polarization relative to the sample and the optical components, so that the terms linear in γ average to zero. We compensate γ to about 10^{-3}, so that the higher-order terms are negligible. As shown in Fig. 1, we have employed a spinning $\lambda/2$ plate to rotate the polarization. When the reflected beam traverses the plate for the second time, the original polarization state is restored, except for the changes introduced by the sample and optical elements and by the error in the $\lambda/2$ plate. Linear birefringence in the stationary elements is compensated by SB_γ. The plate is heated in order to tune its retardation within 0.02%. The reflected light is directed by the beam splitter (BS) into a Soleil-Babinet compensator (SB) and the final detection apparatus. The Soleil-Babinet compensator is operated at a retardation of $\lambda/4$ to observe CD, with its fast axis aligned with the incident linear polarization. As such, it converts an ellipticity into a rotation of the polarization.[6] The linear birefringence term in this rotation averages to zero, leav-

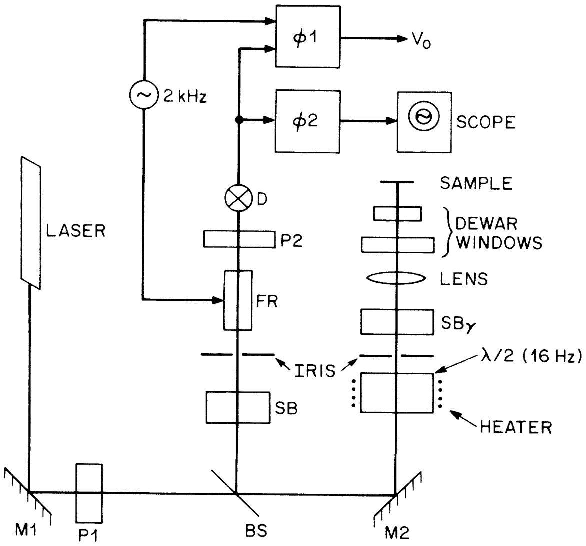

FIG. 1. Schematic of the experimental apparatus employed. Labeling: P, polarizer; BS, beam splitter; M, mirror; SB_γ, Soleil-Babinet compensator used to null the linear birefringence component; L, lens; SB, final Soleil-Babinet compensator normally set to $\lambda/4$; FR, Faraday rotator; P2, output polarizer; D, diode detector. The irises are used to establish autocollimation of the reflection from the sample. The scope monitor enables the accurate nulling of the linear birefringence signal using SB_γ.

ing the nonzero-average value which results from the CD term ϕ. The average rotation of the final polarization, detected by use of a Faraday rotator and a lock-in detector,[7] is then exactly equal to ϕ. The Faraday rotator is driven at 2 kHz, causing the polarization plane to oscillate, and the lock-in detector, operating at 2 kHz also, then provides a signal *linear* in the error angle ϕ of the output polarizer. We used digital averaging to obtain an accuracy of 10^{-5} rad.

There are several sources of systematic error which must be accounted for and eliminated by careful alignment techniques, which will be reported elsewhere.[8] With proper attention, these errors are estimated to be less than 25 μrad.

A complete solution for the response of our measurement apparatus when the reflection coefficients R_+ and R_- are complex shows that the rotation angle ϕ when the output is nulled is just given by $\mathrm{Re}(\Delta R/2\bar{R})$, where $\Delta R = R_+ - R_-$ and $\bar{R} = (R_+ + R_-)/2$. Since the signal is thus proportional to the fractional change in R, it may be more sensitive for thin layers than the transmission technique which has been attempted by other workers.[9]

The samples chosen for our initial study were 500-Å thin films of $\mathrm{YBa_2Cu_3O_{6+x}}$ epitaxially grown on MgO(100) substrates by molecular-beam epitaxy using an activated oxygen source as previously described.[10] X-ray diffraction showed that the samples are (001) oriented with a mosaic spread less than 0.3°. The cleaved MgO substrates typically exhibited cleavage steps 50–100 μm in width. Impurity phases were below detection by x-ray diffraction. The grain sizes of the films are on the order of a few thousand Å to 1.0 μm based on scanning electron microscopy examination. Polarizing microscope examination revealed structure on a 1–2-μm scale, thought to represent the crystal grains. Although not measured in the present samples, we believe the twin domain size to be near 200 Å, on the basis of previous work. The superconducting $R=0$ transition temperatures vary in range from 88 to 86.5 K, with a typical (10%–90%) width of 0.7 K. The normal-state resistivity ρ(300 K) is 190 $\mu\Omega$ cm, and ρ(100 K) is 68 $\mu\Omega$ cm. Critical current densities are over 1×10^6 A/cm^2 at 77 K. The choice of a thin film was dictated by several considerations, including surface quality, flatness, and the ability to probe the entire sample thickness optically. The latter ensures correspondence between our measurements and measurements of bulk superconducting properties on the same sample, such as a Meissner fraction. Moreover, if broken parity and time-reversal symmetry were to occur, the planes could be aligned ferromagnetically or antiferromagnetically (AFM). In the event of AFM alignment, we anticipate that the cancellation of the signal from several planes of a film would be less perfect than in a bulk crystal, providing a more obvious signature of the effect.

The sample was glued to a Si (111) mounting plate, which served as an *in situ* calibration standard for $\phi = 0$. The magnetic susceptibility χ_m of the sample was monitored using excitation and pickup coils behind the silicon plate. A laser power of 2–4 mW (5145 Å) had no noticeable effect on this signal.

Results are shown in Fig. 2, where we plot $\sigma_\phi = \langle[\phi(x,y) - \bar{\phi}]^2\rangle^{1/2}$. The data shown were obtained in zero field. The experiment is carried out by performing individual measurements of ϕ at a series (10–25) of positions x,y on the sample, typically separated by 100 μm. The laser-spot diameter is estimated at 20 μm (aperture 2.5 mm). At each position, we first optimized the reflected intensity by a minor adjustment of the lens,[11] then adjusted SB_y to minimize the diode monitor ac signal at the plate rotation frequency. The current I in a second winding of the Faraday rotator was adjusted to give $V_0 = 0$. Since $d\phi/dI$ is calibrated accurately, this provides an absolute measure of ϕ, independent of the reflected intensity. The measurements of $\phi(x,y)$ obtained in this manner were then analyzed to obtain the average value $\bar{\phi}$ and the standard deviation σ_ϕ.

In zero field the average value $\bar{\phi}$ was within error of zero. In a small external field (20 G) we have observed some hint of a response in $\bar{\phi}$ quite close to the variance of

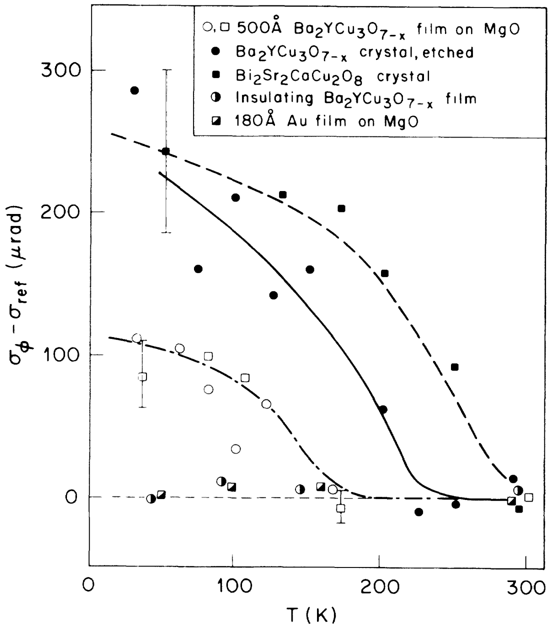

FIG. 2. Standard deviation of the point-to-point variation in ϕ for the samples indicated. The standard deviation σ_ϕ is proportional to the single-domain CD value and to the average domain size. Note that the onset is at a higher temperature for $\mathrm{Bi_2Sr_2CaCu_2O_8}$ (long-dashed line) than for $\mathrm{YBa_2Cu_3O_{7-x}}$ (solid line), and that both of these bulk samples show a larger magnitude for the effect and a higher onset temperature than for the films (dash-dotted line). All lines are guides to the eye. Error bars are shown on representative points only, for clarity. In general, the uncertainty in σ_ϕ is 15%–20% of the value shown.

the mean. However, definitive measurement of the field response must await experiments at higher field, or with better statistics.

In the absence of CD domains, σ_ϕ should be just the instrumental background noise. In the presence of chiral domains, though, the signal ϕ will fluctuate with an addition variance $\sigma_\phi = \phi_0/\sqrt{N}$, where ϕ_0 is the single-domain CD value and N is the number of independent domains contained on average within the laser spot. If the domains are isotropic in the plane, of average radius r, then we expect $\sigma_\phi \sim \phi_0 r/d$, where d is the laser spot size.

The results displayed in Fig. 2 (open symbols) indicate clearly the presence of a CD signal. It appears on cooling in the vicinity of 200 K, and remains relatively unaffected by passage through T_c. We have demonstrated that it is unaffected by small fields ($\sim$20 G) of either sign, and that it decreases as expected when the spot size is increased by aperturing the beam.

Additional experiments have been performed in well-characterized bulk samples. Data are shown in Fig. 2 for bulk single crystals of $YBa_2Cu_3O_{7-x}$ (etched surface[12]) and $Bi_2Sr_2CaCu_2O_8$. Both samples show similar evidence of CD, albeit somewhat larger in size than in the films and with different onset temperatures. The larger signal could be attributed either to a difference in domain size relative to the film samples or to the fact that our optical penetration depth of about 1000 Å exceeds the film thickness, so that the amount of material probed in the bulk crystal is nearly twice as large. (The increased material would only provide a larger signal if the interplanar alignment of the moments is ferromagnetic.) The $YBa_2Cu_3O_{7-x}$ sample shows a single, very narrow superconducting transition at 92 K, while the $Bi_2Sr_2CaCu_2O_8$ sample shows two steps in its susceptibility curve, at 87 and 65 K, manifesting the typical two-phase nature of this material. The $YBa_2Cu_3O_{7-x}$ sample shows a Meissner fraction of a few percent, while the $Bi_2Sr_2CaCu_2O_8$ samples gives $x_M \sim 28\%$, measured with the field nearly parallel to the planes.

The signal has been observed in all superconducting materials studied, with the exception of one. In that case, subsequent SQUID susceptometer measurements showed that the film possessed zero Meissner fraction, when measured with a 50-G field aligned nearly parallel to the Cu-O planes. In contrast, the film shown as the open squares in Fig. 2 gives a Meissner fraction in excess of 80%, under the same conditions, although the transition is significantly broadened in this case, perhaps by interface strain effects. The other film shown there was not measured for a Meissner fraction.

The final experimental result reported here is the disappearance of the circular dichroism signal in a Y-Ba-Cu-O film transformed into insulating $YBa_2Cu_3O_6$ by a brief anneal in flowing nitrogen at 450 °C. Prior to the anneal the CD signal in this sample was checked at low temperature and found to give a variance σ_ϕ comparable to that shown as an open circle and an open square in Fig. 2. Clearly (Fig. 2) there is no CD observed in the insulating material.

Naturally, the possibility of artifactual signals is a source of great concern in such an experiment. Artifacts could stem from two generic sources: (i) the measurement technique and (ii) the samples. In order to check the first possibility, we have made complete temperature scans on (i) a polished silicon sample and (ii) a gold film (180 Å) deposited on an MgO substrate from the same batch. Both sets of data show a low, temperature-independent value of σ_ϕ (the latter set is shown in Fig. 2).

The possibility of sample artifacts is more difficult to address. The variety of samples which we have studied give us confidence that the effect is intrinsic to the cuprate system, but does not alone allow us to eliminate the possibility of some ubiquitous impurity phase which might possess magnetic order and could give rise to such a signal. Moreover, the disappearance of the signal in an insulating $YBa_2Cu_3O_6$ sample provides some evidence that the CD is related to the carriers. The fact that the signal vanishes is strong evidence that we are, in fact, observing a CD signal from the $YBa_2Cu_3O_{7-x}$ itself. Nevertheless, we cannot exclude the possibility that some other properties of an impurity phase may be changed at the same time as the oxygen stoichiometry. This possibility, which would indeed require a rather extreme coincidence of material behavior, can only be addressed by extensive further studies in the best possible superconducting materials, from as wide a variety of sources as possible.

Parity violation together with spatial inhomogeneity could cause a nonzero ϕ in our experiment. In order to understand this, let us write the reflection process as $\hat{x} \pm i\hat{y} \rightarrow A_\pm(\hat{x} \pm i\hat{y}) + B_\pm(\hat{x} \mp i\hat{y})$, in an obvious notation. In the simple reflection process considered above, where right-handed light becomes left handed on reflection, we have simply $B_\pm = 0$. However, in an inhomogeneous material with broken parity the situation may be more complex. For example, in a cholesteric liquid crystal[13] it is possible to obtain $B_+ = 1$ and $B_- = 0$ when the incident wavelength matches the helicity of the molecule. In any material with time-reversal invariance, $A_+ = A_-$, as may be seen by a simple argument involving reversal of source and detector when time is reversed.[14] We have evaluated the effect of $B_\pm$ on our observed signal,[8] and we find a term of the form $|B_+|^2 - |B_-|^2$ which contributes to the observed ϕ. If we write the reflected field $\mathbf{E}_r$ in terms of the incident field $\mathbf{E}_i$ as $E_r^\alpha = \chi_{\alpha\beta} E_i^\beta$, where the matrix χ has the property $\chi_{\alpha\beta} = (\chi_{\beta\alpha})^*$ for time reversal, then the conditions required for $B_+ \neq B_-$, are just (i) $\chi_{11} \neq \chi_{22}$ and (ii) χ not diagonalizable by a rotation. The first condition requires local symmetry lower than cubic while the second requires spatial dispersion in the dielectric properties along z. (Note that by a rotation we can always obtain $\chi_{12} = -\chi_{21} = i\chi_4$. This imaginary off-diagonal term requires spatial dispersion or nonlocality in the dielectric tensor.)

Although the *B*-reflection process can thus contribute to ϕ, we regard it as an unlikely explanation of our data. There are indeed sources of helicity in our materials. In an epitaxial film the twin domains are constrained to a tetragonal structure at the interface, while in the bulk orthorhombic material they do not lie exactly at right angles. Hence, a helical index inhomogeneity related to the twinning could occur in the film. A similar effect in the bulk crystal could stem from layering of twin domains. This rotation is, however, a small effect (about 1°) and it has a characteristic relaxation length far smaller than the optical wavelength. The orthorhombicity is also not temperature dependent in the range studied here. Moreover, these same twin boundaries exist at room temperature, where σ_ϕ drops to the background value. Therefore, it seems unlikely that they could be responsible for our signal.

On the other hand, our results appear to conflict with other measurements. Although it is not possible to relate σ_ϕ directly to an internal field, the various other experimental probes which should manifest any local magnetic field, such as muon spin rotation, NMR, and susceptibility, show no evidence for a magnetic order.[15] Unless other signatures of magnetic order are discovered, the possibility remains that some effect related to spatial variation and parity violation alone could be contributing, via the $B\pm$ terms. It may be possible to distinguish the $B\pm$ reflections from the normal $A\pm$ ones by suitable changes in the optical configuration. Such experiments are planned for the near future. We note, however, that CD can exhibit strong resonance effects.[16] The other techniques employed explore the low-energy limit. It is certainly possible that this fact could explain the difference in the results obtained. Nevertheless, given the startling nature of our results, we feel that they must be considered preliminary until they have been reproduced by other workers and until a complete picture has emerged encompassing all the relevant experiments. Moreover, although anyon theories provided the original motivation for this work, there is nothing at this time to tie the observed CD signal to anyons definitively. Thus, we must continue to consider other possible explanations.

In summary, the data in Fig. 2 constitute the first experimental evidence for circular dichroic reflection from oxide superconductor samples. Although materials' artifacts remain a significant concern, we conclude that the σ_ϕ signal we observe is probably the signature of a phase transition to a chiral phase. No conclusion is possible regarding internal magnetic fields. The size of the signal observed is quite surprisingly large, suggesting that the distortion responsible for the signal must be ordered in a "ferro" sense from one plane to the next. The signal is stronger in bulk material than in the films, and appears to correlate in our measurements with the presence of superconductivity and with an observable Meissner fraction. This correlation lends support to our interpretation that the CD signal results from the superconducting material itself. We emphasize, though, that although our data are suggestive, the observed effect is not linked definitively to anyons, and may be amenable to explanation in more conventional terms.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986); M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).

[2] See papers in *Novel Superconductivity,* edited by V. Kresin and S. A. Wolf (Plenum, New York, 1987), Sec. V, pp. 295–581.

[3] R. B. Laughlin, Science **242**, 525 (1988).

[4] B. I. Halperin, J. March-Russel, and F. Wilczek, Phys. Rev. B **40**, 8726 (1989).

[5] X. G. Wen and A. Zee, Phys. Rev. B **41**, 240 (1990).

[6] If this compensator is removed, or set to zero retardation, our signal becomes proportional to the circular birefringence, $R_\pm = Re^{\pm i\phi'}$. In the present work we have focused on the circular dichroism effect, since the uncompensated linear *dichroism* makes a much larger spurious contribution to the circular birefringence, due to higher-order terms, than it does to the circular dichroism.

[7] J. F. Dillon, Jr., E. M. Gyorgy, F. Hellman, L. R. Walker, and R. C. Fulton, J. Appl. Phys. **64**, 6098 (1988).

[8] K. B. Lyons, J. F. Dillon, Jr., and M. McGlashan-Powell (to be published).

[9] A. Kapitulnik *et al.* (private communication). In this case, the signal is proportional to $(\eta_+ - \eta_-)d$, where η is the real part of the refractive index and d is the layer thickness.

[10] J. Kwo, M. Hong, D. J. Trevor, R. M. Fleming, A. E. White, R. C. Farrow, A. R. Kortan, and K. T. Short, Appl. Phys. Lett. **53**, 2683 (1988).

[11] We note that adjustment of the lens is made necessary by the cleavage steps on the MgO surface. The exact manner in which the laser spot falls on the steps influences the direction of the reflected spot, typically by a few milliradians. This leads to a small spurious signal ϕ. The additional noise imparted by this surface morphology is evident in the results for the Au film in Fig. 2, in which an MgO substrate with similar step structure was employed.

[12] D. J. Werder, C. H. Chen, M. Gurvitch, B. Miller, L. F. Schneemeyer, and J. V. Waszczak, Physica (Amsterdam) **160C**, 411 (1989).

[13] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974), Chap. 6.

[14] We are indebted to B. Halperin for this observation.

[15] R. F. Kiefl *et al.* (to be published).

[16] K. H. Clemens and J. Jaumann, Z. Phys. **173**, 135 (1963).