Circular dichroism observed in bismuthate superconductors

K. B. Lyons, J. F. Dillon, Jr., E. S. Hellman, E. H. Hartford, and M. McGlashan-Powell
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 8 August 1990)

We report observation of circular dichroism (CD) in reflection from two bismuthate superconducting thin films, rubidium barium bismuthate. This signal is similar to that recently reported in cuprate materials, with the exception that one sample shows a dramatic rise in the observed CD variance at the superconducting transition. These results suggest that a mechanism other than anyons, and thus perhaps unrelated to the superconductivity mechanism itself, might be necessary to explain the CD observed.

We have recently reported[1] measurements of a nonzero circular dichroism (CD) in the reflection of light incident normally on superconducting cuprate films and bulk crystals. Interest in such an experiment has been expressed in the theoretical paper of Wen and Zee.[2] A subsequent CD measurement[3] on untwinned samples showed much larger CD values. Although these results suggest the applicability of recent theories[4] of the high-temperature superconductors which predict the breakdown of time-reversal symmetry (T) and parity (P), we noted in that report the absence of corroborating evidence from other relevant experimental techniques, including notably muon spin rotation (μSR) and NMR, which should be sensitive to T breaking. Furthermore, CD measurements at a photon energy of 1 eV in similar samples have shown a null result.[5] Since the so-called "anyon" theories are predicted based on the two-dimensional nature of the cuprates, the question immediately arises as to whether a similar effect might be observed in the doped bismuthates, which are cubic. In the present report we discuss preliminary measurements on cubic $Ba_{1-x}Rb_xBiO_3$ films, where we find not only that the effect exists but also, for a single sample, we find a large change in the observed CD magnitude precisely at T_c. Although these results suggest that the broken symmetry reflected in the circular dichroism may be related to the superconductivity, they also indicate that the theoretical models[4] which depend on the two dimensionality of the system are not a complete description of the CD mechanism. This work thus suggests that these theories must be revised to include three-dimensional materials, if that is possible, or that some other mechanism for the CD phenomenon should be sought for the bismuthates, and perhaps for the cuprates as well.

The experimental apparatus is essentially that previously described.[1] We utilize a rotating half-wave retardation plate to enable complete discrimination against linear birefringence and dichroism effects. The experiment is carried out at every temperature by measuring the CD rotation angle ϕ_{CD} at a set of spots on the sample (laser focus spot size $\sim 20\ \mu$m). The spots are selected to provide high-quality reflection (avoiding cleavage steps in the substrates) and are spaced roughly 100 μm apart. As expected in a zero-field experiment ($H<0.5$ G) the measured values of the circular dichroism average approximately to zero. The quantity we report is σ_ϕ, the variance in these measured values. As we have discussed previously[1] the presence of circular dichroism domains of size d, with a single-domain dichroism value of ϕ_0, will result in a variance $\sigma_\phi = \phi_0 d/a$, when probed with a laser spot diameter a. The laser spot diameter was not varied during the measurements reported here. The observability of this variance contribution will be governed by the random uncertainty in the circular dichroism measurement, which places a practical lower limit of about 20 μrad on the variance which can be detected.

Some minor improvements in the alignment process have been added, and a complete mathematical description of the important error terms has now been achieved.[6] The fundamental results may be summarized as follows. Any reflection process may be described in terms of four reflection coefficients, depending on the initial and final polarization states. If we denote the polarizations $\mathbf{x} \pm i\mathbf{y}$ as $\mathbf{e}_\pm$, then we can describe the reflections of incident $\mathbf{e}_\pm$ light as

$$\mathbf{e}_\pm \rightarrow A_\pm \mathbf{e}_\pm + B_\pm \mathbf{e}_\mp \ .$$

In complete generality[7] for a material which possesses time-reversal symmetry, we must have $A_+ = A_-$. For simple homogeneous materials, $|B_+| = |B_-|$, even in the presence of linear birefringence or dichroism. However, inhomogeneity along the optic axis can cause nonequality of $B_\pm$. The importance of this fact, as we have shown previously,[1,6] is that the rotation angle observed in our experiment is given by

$$\phi_{CD} = (|A_+|^2 - |A_-|^2 + |B_-|^2 - |B_+|^2)/(|A_+|^2 + |A_-|^2) \ , \quad (1)$$

where we have assumed ϕ_{CD} small. Thus, the A and B terms enter in a nearly equivalent way into the final measurement. We note the absence of B terms in the denominator of (1).[6] For a homogeneous medium with time reversal violated, where $A_\pm = A \pm \delta$ and $|B_+| = |B_-|$, we obtain $\phi \cong \mathrm{Re}(2\delta/A)$. Although we have argued[1] that the difference between $|B_+|$ and $|B_-|$ should be small, there is no experimental way to distinguish the A and B

terms in the CD measurement using this rotating plate technique. Moreover, one mechanism for such a difference, namely, the layering of twin domain boundaries in different orientations in the sample, would disappear in the cuprate insulator, since the orthorhombicity vanishes.[1] Thus, although the reported results in the cuprates suggest the possibility of time-reversal violation, they do not prove it.

In this Brief Report, we describe measurements performed on $Ba_{1-x}Rb_xBiO_3$ films grown on MgO substrates, by molecular-beam epitaxy.[8] Higher substrate temperatures than used previously were necessary to obtain (100) orientation on the MgO.[9] The substrate was rotated during growth to ensure compositional uniformity. The superconducting $Ba_{1-x}Rb_xBiO_3$ samples have phase purity and superconducting properties which fall well short of those of the cuprate samples previously studied. A significant impurity phase RbO_2 can appear in superconducting films. The value of T_c measured resistively exceeds by as much as several degrees that measured by ac magnetic susceptibility. Finally, dc measurements using a superconducting quantum interference device (SQUID) show shielding behavior that is poor to nonexistent, and no observable Meissner effect is present. Naturally, since far less total effort has been expended on the bismuthate materials worldwide, it is not surprising that the quality of the available material falls short of what might be preferred. It is important to note, though, that no magnetic cations are present and that the only known magnetic impurity phase is RbO_2, which becomes antiferromagnetic[10] at low temperature ($T_N=15$). Although this RbO_2 phase is a potentially troublesome complication, it is difficult to envision that it or some other accidental phase could provide a magnetic CD signal near or above $T_c \sim 20$ K. It should also be noted that in the cubic perovskite structure of $Ba_{1-x}Rb_xBiO_3$ the mechanisms which could lead to a significant $(|B_+|^2-|B_-|^2)$ term should not be present in the same way as in the orthorhombic 1:2:3 materials.

Specifically, two samples were employed. Sample 1, 2000 Å thick, showed a resistive transition 3 K wide, reaching zero resistance at 20 K, and a somewhat smeared transition in ac susceptibility beginning near 18 K. It had a metallic normal state resistivity. No measurable dc shielding or Meissner effect were observed in this sample. X-ray analysis shows an observable amount of an RbO_2 phase. Sample 2, 1500 Å, showed a semiconducting normal state resistivity, with a transition beginning near 30 K and reaching zero resistance around 22 K. It shows a rather sharp transition in ac susceptibility around 20 K. SQUID measurements show dc shielding currents developing also near 20 K, but no Meissner effect could be observed. X-ray data shows RbO_2 less than one-tenth of that in the first sample. The composition of the films was measured by Rutherford backscattering to be $Rb_{0.25}Ba_{0.23}Bi_{0.52}$ (sample 1) and $Rb_{0.21}Ba_{0.27}Bi_{0.52}$ (sample 2). The excess Rb in sample 1 results in the RbO_2 impurity phase. Neither sample shows any evidence of crystal grains in other than (100) orientation in the x-ray data. As we shall see, these two samples show rather different results, although both show evidence of a CD signal. Both samples had optical transmission close to that previously employed, about 40% at 5145 Å, while the reflectivity, near 10%, was somewhat lower than the 1:2:3 films previously studied.

As discussed above, the experimental results are reported here in terms of σ_ϕ. The results for sample 1 are shown in Fig. 1. There are several noteworthy features of these data. First is the fact that the high-temperature portion of the curve ($T > T_c$) strongly resembles that observed in the cuprate materials,[1] both in magnitude and temperature dependence. The behavior at T_c, though, is strikingly different. On cooling into the superconducting phase we observe a severalfold increase in σ_ϕ, whereas no change (outside the 20% error bar) was observed in any of the cuprate materials at T_c. We locate T_c for this purpose by use of an *in situ* ac susceptibility probe, consisting of a balanced coil pair[11] positioned behind the sample. In these measurements we traversed T_c a total of six times (three round trips) in steps of decreasing size. The sample was not cycled above 40 K during this particular set of measurements. In the final pair of measurements, a temperature change of only 1.5 K was employed, which is essentially the observed width of the transition. In every case, we found a dramatic difference in the spatial variation of the CD signal above and below T_c. A blowup of the transition region is included in Fig. 1 as an inset, showing both the σ_ϕ and χ_n values. Finally, we note that the value of σ_ϕ observed below T_c is 2–3 times as large as that observed in the cuprate materials with comparable focusing conditions.

The results in sample 2, shown in Fig. 2, are not the same, particularly near T_c. Although the high-temperature behavior is similar, the low-temperature behavior seems to suggest a two-plateau curve, with the

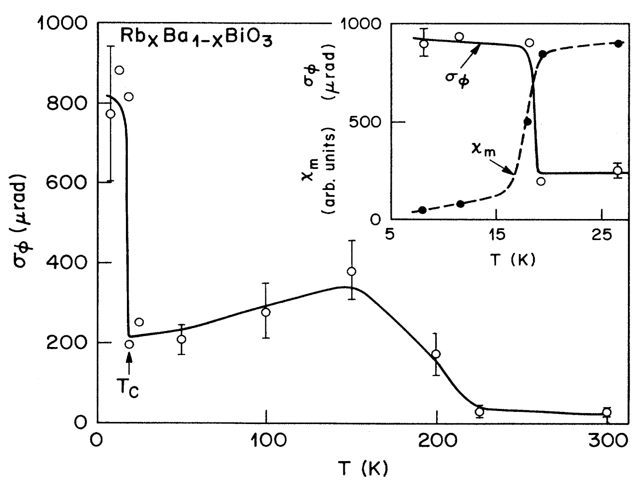

FIG. 1. Circular dichroism in reflection, reported as the variance σ_ϕ, for a superconducting sample of $Ba_{1-x}Rb_xBiO_3$ (sample 1 in the text). The dashed line in the inset shows the actual χ_m curve measured on a separate run, while the values obtained at the points corresponding to the σ_ϕ measurements (open circles) are shown by the solid dots. Solid lines are guides to the eye.

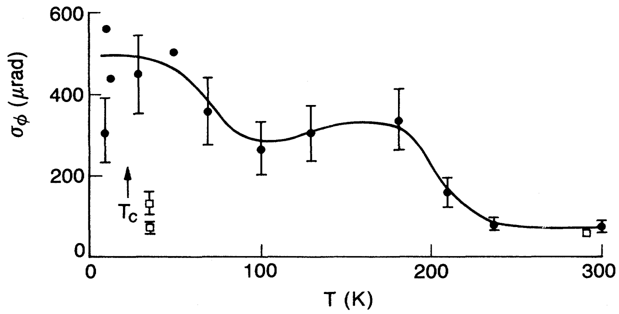

FIG. 2. Measured values of σ_ϕ for sample 2 (solid dots), nominally the same material as in Fig. 1, with somewhat different superconducting properties (see text). Note the absence of any observable anomaly at T_c. The squares show corresponding measurements on an insulating sample.

second plateau being reached on cooling to about 50 K. The plateau structure is near the level of the noise, and in fact is consistent with the absence of temperature dependence below 200 K. No further increase at T_c is evident. The maximum value observed for σ_ϕ is considerably smaller.

A third $Ba_{1-x}Rb_xBiO_3$ sample, grown at $x=0.3$ to produce an insulating material, was also measured to provide a baseline for the data. Measurements were only performed at a few temperatures after it was ascertained that no temperature variation was evident. These points are included in Fig. 2. The value of $\sigma_\phi \sim 60$ μrad obtained in this case is nearly the same as that obtained from a polished silicon surface used as a reference inside the dewar.

As noted in the Introduction, the presence of a CD signal is entirely unexpected for the bismuthates in the context of the theory of anyon superconductivity, given the cubic symmetry of $Ba_{1-x}Rb_xBiO_3$. Furthermore, there is no known structural change which occurs at T_c to provide any explanation for the abrupt change in σ_ϕ observed in sample 1. Hence, while the results in both samples are puzzling, the T_c anomaly in sample 1 is doubly so. Although neither sample shows clear evidence of bulk superconductivity, dc measurements on sample 1 do not even manifest persistent shielding currents, suggesting that only filamentary superconduction is present. This possibility is also indicated by critical current measurements on a sister sample, which give $J_c \sim 1$ A/cm^2, consistent with the inability to detect dc shielding currents. The possibility remains that the observed CD signal is in some way related to the nonuniform nature of this superconducting material. On the other hand, the CD measurements in the insulating $Ba_{1-x}Rb_xBiO_3$ material ($x=0.3$) show that the nonzero CD is associated, for whatever reason, with the presence of superconductivity.

We shall not attempt here to formulate an interpretation of these observations. We report them simply to draw attention to evidence that the anyon superconductivity theories, in their present forms, do not describe the data from CD measurements in these bismuthate samples. The sudden change in σ_ϕ at T_c in one sample certainly suggests that the CD may be related to the superconductivity mechanism, but the nature of that relationship remains obscure at this writing. We certainly cannot exclude the possibility that a structural phase transition, heretofore unobserved, might be responsible, or that the superconducting transition might influence σ_{CD} via a change in the environment of magnetic impurities. Clearly, it is now important that efforts be made on various fronts to improve the material quality of the samples available in order to exclude possible materials artifacts, and that measurements be made on other members of the bismuthate family. Both efforts are presently under way in our laboratory. Lastly, although there is no certainty that the origin of the effect we report here is the same as in the cuprates, these results suggest that alternative explanations of the observed CD effect should be considered in that case as well.

We are indebted to A. P. Ramirez for assistance with sample characterization as a part of this study.

---

[1]K. B. Lyons, J. Kwo, J. F. Dillon, Jr., G. P. Espinosa, M. McGlashan-Powell, A. P. Ramirez, and L. F. Schneemeyer, Phys. Rev. Lett. **64**, 2949 (1990).

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

[3]H. J. Weber *et al.*, Solid State Commun. **76**, 511 (1990).

[4]R. B. Laughlin, Science **242**, 525 (1988); Bertrand I. Halperin, John March-Russel, and Frank Wilczek, Phys. Rev. B **40**, 8726 (1989).

[5]S. Spielman, *et al.*, Phys. Rev. Lett. **65**, 123 (1990).

[6]K. B. Lyons, J. F. Dillon, and M. McGlashan-Powell (unpublished).

[7]B. I. Halperin, Proceedings of the International Seminar on the Theory of High Temperature Superconductivity, Dubna U.S.S.R. (Joint Institute of Nuclear Physics, Dubna, 1990).

[8]E. S. Hellman, E. H. Hartford, and R. M. Fleming, Appl. Phys. Lett. **55**, 2120 (1989).

[9]E. S. Hellman and E. H. Hartford, J. Vac. Sci. Technol. B **8**, 332 (1990).

[10]A. Zumsteg, A. Ziegler, W. Kanzig, and M. Bosch, Phys. Condens. Matter **17**, 267 (1974).

[11]A. T. Fiory, A. F. Hebard, P. M. Monkiewich, and R. E. Howard, Appl. Phys. Lett. **52**, 2165 (1988).