Circular Dichroism in Angle-Resolved Photoemission Spectra of Under- and Overdoped Pb-Bi2212

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We use angle-resolved photoemission with circularly polarized excitation to demonstrate that in the 5×1 superstructure-free $(Pb, Bi)_2Sr_2CaCu_2O_{8+\delta}$ (Pb-Bi2212) material there are no signatures of time-reversal symmetry breaking in the sense of the criteria developed earlier [Kaminski *et al.*, Nature (London) **416**, 610 (2002)]. The dichroic signal retains reflection antisymmetry as a function of temperature and doping and in all mirror planes, precisely defined by the experimental dispersion at low energies. The obtained results demonstrate that the signatures of time-reversal symmetry violation in pristine Bi2212, as determined by angle-resolved photoemission spectroscopy, are not a universal feature of all cuprate superconductors.

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The variety of specific points, lines, and regions in the "normal state" part of the phase diagram of the high-temperature superconductors clearly demonstrates not only its complexity but also the absence of its detailed understanding [1]. It is therefore important to realize which of them are really universal boundaries of particular phases and which just designate intermediate states with properties defined by the proximity to the well established phases such as superconductivity. A recent angle-resolved photoemission spectroscopy (ARPES) study [2] found evidence of time-reversal symmetry breaking below the so-called T^* line, implying the existence of a well defined phase transition in underdoped cuprates. However, in the same set of experiments it was shown that the violation of the time-reversal symmetry is not peculiar only to the pseudogap regime but persists well in the superconducting state. This latter observation suggests that the detected symmetry breaking could, in principle, originate from the superconducting state and then be the primary cause of the effect in the pseudogap regime. This uncertainty calls for further experimental investigations and can be clarified if the superconducting state of the overdoped samples is studied in the same manner. Moreover, the importance of the issue appeals to the confirmation of already existing data since the observation of the effect is an extremely demanding experiment [2,3] in which a number of artifacts should be ruled out before one can state that exactly the time-reversal symmetry breaking is responsible for the nonvanishing dichroism in the mirror plane. It was already suggested [4] that the $\approx 3\%$ asymmetry effect observed in the underdoped samples can be explained by the changes of the well known incommensurate modulation (reported in Ref. [2] to be also of the order of 3%) as a function of temperature. Therefore, analogous experiments carried out on the systems with reduced interference of the temperature-sensitive structural modifications together with the development of an improved experimental methodology aiming at more precise and reliable investigation of circular dichroism effects in low energy photoemission would be of special interest today.

In this Letter we present the results of the ARPES investigation of the $(Pb, Bi)_2Sr_2CaCu_2O_{8+\delta}$ (Pb-Bi2212) cuprates known to have no 5×1 superstructure. We demonstrate that the reflection antisymmetry of the dichroic signal with respect to the mirror planes remains insensitive to both temperature and doping level.

The experiments were performed at the 4.2R beam line "Circular Polarization" of the ELETTRA storage ring using approximately 90% circularly polarized (CP) light from the elliptical wiggler undulator. Spectra were collected in the angle-multiplexing mode of the SCIENTA SES-100 electron-energy analyzer. The overall average resolution in $(\mathbf{k}, \omega)$ space was set to $0.01\ \text{Å}^{-1} \times 0.02\ \text{Å}^{-1} \times 40$ meV. An essential advantage of this experimental setup is that no mechanical movement is involved in the process of switching the helicity of the incoming radiation. Only the direction of the current in the coils of the wiggler undulator needs to be reversed, which takes approximately 30 s. This enables the successive recording of the spectra using the light of both polarizations with the other experimental parameters remaining unchanged. Direct imaging of the beam spot (typical linear size $\sim 300\ \mu$m) on the sample surface using the transmission mode of the same electron-energy analyzer has demonstrated its perfect ($< 10\ \mu$m) spatial stability with respect to multiple switching of the helicity. We note here that such experimental conditions are obviously more favorable for the dichroism studies than those reported in Ref. [2], where not only the polarizer

is rotated resulting in the residual beam movement but also the experimental chamber needs to be adjusted every time the helicity is changed.

High-quality single crystals of 5×1 superstructure-free, underdoped ($T_c = 77$ K) and overdoped ($T_c = 70$ K) Pb-Bi2212 were mounted on the three-axis stepper motor driven cryomanipulator allowing a precise (0.1°) positioning of the sample with respect to the analyzer's entrance slit. The spectroscopic evidence for the pseudogap in our underdoped samples can be found in Ref. [5]. We note that at present we cannot rule out the existence of the pseudogap also at room temperature, but, if present, its magnitude is definitely smaller than at 120 K. Alignment of the crystals was done by recording characteristic spectra with pronounced **k** dependence. The stability of the sample orientation was further controlled by a digital camera with a sensitivity to the relative movement of the sample of the order of 0.1°. The excitation energy was chosen to be $h\nu = 50$ eV for two reasons: (i) the emission from the antibonding band is strongly enhanced near the $(\pi, 0)$ point in comparison with that from the bonding band, thus effectively reducing the number of features in the spectra [6]; (ii) the $(3\pi, 0)$ point becomes accessible in normal incidence geometry at an emission angle of 45°. Intensity variations of the synchrotron radiation were controlled by continuously monitoring the ring current. If jumps of more than 1% were observed during the data acquisition, measurements have been repeated. The data were collected at 300, 100, and 30 K.

The basic idea of our approach is the same as was previously suggested and experimentally tested [2,3], but there are important differences, which we discuss in the next paragraph. According to the proposed criterion one needs to control the value of the dichroic signal corresponding to the emission within a mirror plane. If this signal is zero, the time-reversal symmetry is preserved; if not—it is broken. At that, vectors of incidence and emission, as well as normal to the sample surface, should lie in this mirror plane. Such significant modification (an earlier proposal can be found in Ref. [7]) of the criterion was required because of the strong dichroism observed in the case when the experimental geometry posesses a "handedness," i.e., when at least one of the three mentioned vectors is not in the mirror plane. Regardless of the origin of such an effect, though argued to be geometric in Ref. [3], it can be used to track down the temperature dependence of the intrinsic dichroism (if any). The geometric effect is odd with respect to the reflection in a given mirror plane, and an intrinsic dichroism, expected to be even, should then result in an effective "rotation" of this mirror plane upon entering the pseudogap regime of underdoped samples, as was observed for pure Bi2212 in Ref. [2], where the corresponding angle was estimated to be 2.3°.

To test the time-reversal invariance of the electronic states in Pb-Bi2212, we record the photoemission intensity simultaneously for **k** vectors from the cuts crossing the mirror plane at a right angle [see Figs. 1(a) and 1(b)]. Resulting intensity distribution in (k, ω) space, or energy distribution maps (EDM), taken at room temperature using the right-hand (I^+) and left-hand (I^-) CP lights are shown in Figs. 1(c) and 1(d), respectively. One easily notes an asymmetric character of both distributions with respect to the zero **k** values representing the mirror plane. Figures 1(e) and 1(f) show normalized, $(I^+ - I^-)/(I^+ + I^-)$, and simple, $I^+ - I^-$, differences of the EDMs shown above. Here one sees how the dichroic signal is distributed as a function of energy and momentum. Its essentially homogeneous character [Fig. 1(e)] seems to be in agreement with its geometric origin. The main bases of our data analysis are the three types of curves shown in Fig. 2: (i) momentum distribution curves (MDC) corresponding to the total photocurrent [one example is shown as a solid white line in Fig. 2(b)], (ii) integrated normalized difference ($\mathbf{D_N}$) and (iii) integrated simple difference (**D**). MDCs are needed to precisely determine the **k** location of the mirror plane. The other two curves are obtained by integration within the energy interval of −450 to 100 meV of the corresponding $(\mathbf{k}, \omega)$ distributions of the dichroic signal [e.g., shown in Figs. 1(e) and 1(f)].

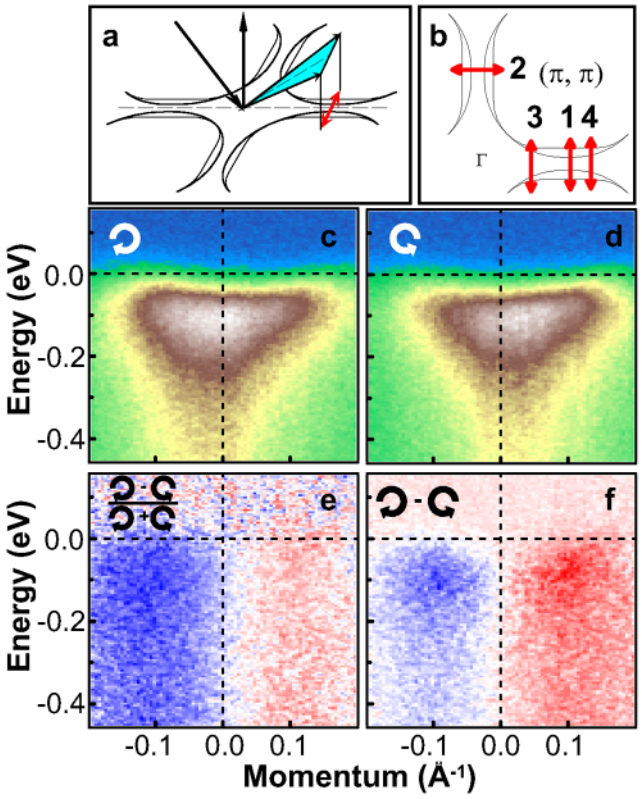

FIG. 1 (color online). (a) Schematic layout of the experiment. (b) Cuts in **k** space corresponding to the recorded spectra. (c),(d) EDMs taken using the light of (c) positive and (d) negative helicity. (e) The normalized difference. (f) The difference.

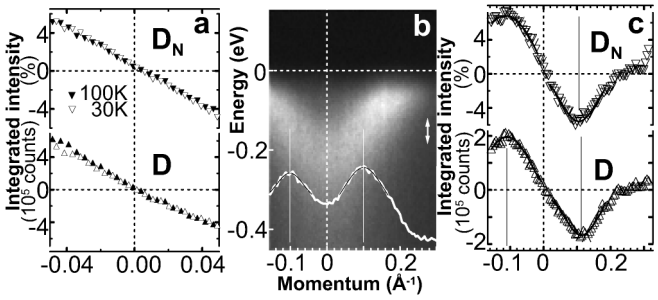

FIG. 2. Overdoped sample. (a) Dichroic signals corresponding to cut 4 [see Fig. 1(b)] at 100 and 30 K. (b) EDM taken along cut 3 in the superconducting state and MDC (white line, obtained by the integration of the spectral weight within the energy range shown by the double-headed arrow) used to determine the origin of the momentum scale. (c) Corresponding dichroic signals with pronounced **k** dependence, which allows a self-check procedure.

We stress two important points here. We *first* determine the position of the mirror plane with the precision of 0.002 Å^{-1} from considering MDCs of the total distribution [Fig. 2(b)] and then plot $\mathbf{D_N}$ and $\mathbf{D}$ in these coordinates. In other words, we believe that the best accuracy in alignment could be achieved using "internal" reference points, such as experimental dispersion derived from the MDCs maxima of the total spectral weight. It is worth noting that these reference points are obtained in static conditions, i.e., without any movement of the sample or the analyzer, which is ruled out when using a smaller detector at lower photon energies as in Ref. [2], where neither the procedure itself nor the accuracy of the momentum scale determination was reported.

The second point is that now, when we have recorded the signal in a relatively wide momentum interval, one easily notices the nonmonotonic character of both $\mathbf{D_N}(\mathbf{k})$ and $\mathbf{D}(\mathbf{k})$ dependencies [Fig. 2(c)]. Locations of the extrema as well as their absolute intensities could be determined with a high precision using a fitting procedure and are symmetric with respect to the origin when the sample is properly aligned. We have systematically studied the line shape of $\mathbf{D_N}$ and $\mathbf{D}$ as a function of misalignments of different types. Both turned out to be extremely sensitive: not only did the curves not pass through the origin imitating the presence of the intrinsic dichroism, but at the same time their maxima and minima were no longer symmetric with respect to zero. This observation opens up an additional possibility to check the reflection invariance of the dichroic signal.

Another important advantage of recording the wide-range dichroic signal follows from the remarkable property of the $D_N = (I^+ - I^-)/(I^+ + I^-)$ function. Its line shape is practically independent of the intensity ratio of the right- and left-hand circularly polarized photon flux, which has defined the accuracy of the experiments in Ref. [2]. Indeed, if α is a factor to account for the different flux of the photons of opposite helicities, for instance, due to the changes of the ring current, then

$$D'_N = \frac{I^+ - \alpha I^-}{I^+ + \alpha I^-} = \frac{D_N + 1 - \alpha + \alpha D_N}{D_N + 1 + \alpha - \alpha D_N}. \quad (1)$$

One can expand D'_N as

$$D'_N = \frac{1-\alpha}{1+\alpha} + \frac{4\alpha}{(1+\alpha)^2} D_N + \frac{4\alpha(\alpha-1)}{(1+\alpha)^3} D_N^2 + \ldots, \quad (2)$$

where, since D_N is usually very small and α is of order of 1, only the first two terms are essential. It is easy to see that deviation of α from unity rescales and shifts only the D_N function along the vertical axis, leaving the opportunity to define **k** locations of the extrema with the same precision. From this observation it follows that one can use the D_N line shape alone to search for the intrinsic dichroism unless the expected effect is of the same magnitude and sign for all k vectors along the studied cut which would contradict theoretical prediction anticipating a maximum at the $(\pi, 0)$ point [3].

Now we apply our approach to check whether there is an effect in the superconducting state of the overdoped sample—the issue that was not addressed before. We compare in Fig. 2 the $\mathbf{D_N}$ and $\mathbf{D}$ curves measured at 100 and 30 K. In this case we observe antisymmetric behavior of both $\mathbf{D_N}$ and $\mathbf{D}$, and it is not sensitive to the temperature [Fig. 2(a)]. We plot the data in a momentum scale, comparable with the one used for the presentation of the data in Ref. [2]. As is seen, the accuracy of our experiment is better and allows one to make a conclusion about the absence of the effect of the mirror plane rotation in the overdoped sample upon entering the superconducting state.

Figures 2(b) and 2(c) illustrate that the additional condition described above is satisfied. Data are taken now along the cut closer to the Γ point, which results in more clearly pronounced extrema of $\mathbf{D_N}$, the momentum location of which we determine by fitting these parts with Gaussians. The left maximum resides at -0.115 ± 0.003 Å^{-1}, whereas the right minimum is at 0.113 ± 0.001 Å^{-1}.

The data recorded on underdoped samples are presented in Fig. 3. The first row shows EDMs of total intensity together with $\mathbf{D_N}$ curves recorded perpendicular to the two mirror planes Γ-$(\pi, 0)$ and Γ-$(0, \pi)$ in the pseudogap state. As seen from Fig. 3(c), the dichroism in the mirror plane is negligible. At zero momentum linear fits cross the vertical axis at 0.16% and -0.41%, respectively, which is within the error bars ($<0.5\%$). These values are even much smaller than the dichroism value of $\sim 4\%$ reported in Ref. [2] for the pseudogap regime. In Fig. 3(d) we compare dichroic signals recorded along cut 3 [Fig. 1(b)] measured at 100 and 30 K, and again, as follows applying both criteria, there is no visible deviation from zero. Figures 3(e) and 3(f) represent the data taken in normal incidence geometry. Because of the relatively large emission angle (45°), reduced "handedness" of the experiment (because of the coplanarity of

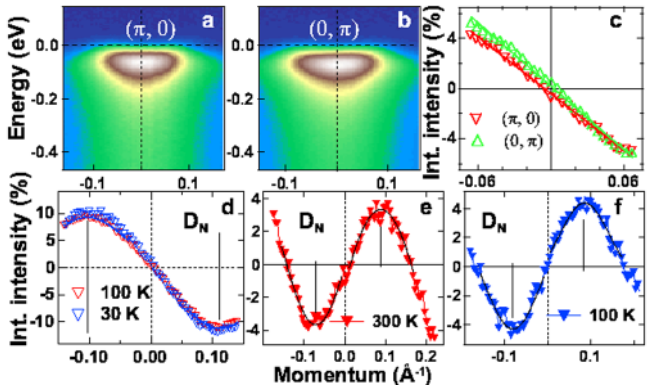

FIG. 3 (color online). (a),(b) EDMs of the total photocurrent along the cuts through the $(\pi, 0)$ and $(0, \pi)$ points (cuts 1 and 2) taken at 100 K and (c) correspondent $\mathbf{D_N}$ curves together with linear fits. (d) $\mathbf{D_N}$ curves for cut 3 measured at 100 and 30 K. (e),(f) Normal incidence $\mathbf{D_N}$ curves taken at 300 and 100 K. For details see text.

three aforementioned vectors), and radial matrix element effects, the signal is weaker and more problematic for the application of the absolute intensity criterion. Linear fits in the vicinity of the zeroth momentum cross the vertical axis at -0.63% and 0.18%, respectively, which is slightly more than experimental uncertainty ($\sim 0.5\%$) for the room temperature curve. This is exactly the case when one can apply additionally the line shape criterion discussed above. Fitting the extrema of the normal incidence curves measured at 300 and 100 K we find that the "zero" is shifted by less than 0.009 Å^{-1} at room temperature and by less than 0.004 Å^{-1} in the pseudogap regime implying that the reason for the small dichroism in the mirror plane is the residual misalignments. A qualitatively similar picture was observed for other underdoped samples (results are not shown).

The accuracy of our experiments could be estimated in two ways. We distinguish between the temperature dependent measurements where error bars are given by the size of the relative shift of the $\mathbf{D_N}$ curve and measurements of a single $\mathbf{D_N}$ curve at a given temperature where the accuracy is defined by the absolute $\mathbf{k}$ value at which the dichroism is zero or by the absolute dichroism value at $\mathbf{k} = 0$. In both cases, typical values are of the order of ± 0.004 Å^{-1}, which in terms of the dichroism is $\pm 0.3\%$ or in terms of the degree of the mirror plane rotation would be $\pm 0.3°$. Note that our additional criterion allows one to identify and account for the major source of the errors—misalignments. In some particular cases [e.g., Figs. 3(e) and 3(f)] the quality of the Gaussian fits defines the precision of the experiment ($\pm$ 0.005 Å^{-1}).

Our attempts to study pure Bi2212 single crystals led us to the following conclusions. Because of the 5 : 1 superstructure present in Pb-free Bi2212 samples, the dichroic signal measured in the $(\pi, 0)$ point already at the room temperature is not equal to zero. According to our measurements, it is $\sim 3.7\%$ and the $\mathbf{D_N}$ line crosses the momentum axis away from the $(\pi, 0)$ point, which is easy to understand since the additional dichroism related to the two diffraction replicas crossing the Fermi level along this cut is not compensated. This is because diffraction replicas originate from the different Brillouin zones where the corresponding photoemission signal is widely known to be different due to the matrix element effects. If one, however, starts to measure the evolution of the dichroism in the point where it is zero at room temperature, i.e., not in the $(\pi, 0)$ point, it is not surprising that at lower temperatures the dichroism can become nonzero. Moreover, this effect will be doping dependent since in the overdoped samples diffraction replicas are less important crossing the Fermi level further away from the $(\pi, 0)$ point than in underdoped samples.

The obtained results do not rigorously disprove the existence of the time-reversal symmetry breaking phase in the pseudogap part of the cuprates' phase diagram. We simply find no experimental evidence for the specific [3] pattern of circulating currents in the studied compounds according to the theoretical proposal and in contrast to the experimental observation of the effect in pristine Bi2212 [2]. One should notice, however, that the reason for nonobservation of the effect can in our case be the domains of the size smaller than 300 μm. While the present results put strong constraints on the possible scenarios involving the circulating currents, in some particular cases the obtained information is not sufficient to make a conclusive statement. For instance, while an antiferromagnetic pattern of currents required by the *d*-density wave instability [8] is invariant upon reflections in the Γ-$(\pi, 0)$ plane, reflection in the Γ-(π, π) plane results in a pattern of currents that can be obtained by shifting the initial one by one unit cell vector (i.e., this plane is a glide plane) and therefore cannot be distinguished from the mirror plane reflection in a photoemission experiment. In this case, perhaps, more detailed knowledge as for the energy and momentum distribution of the dichroic signal is required.

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