Superconductors

Time-reversal symmetry breaking?

Arising from: Kaminski, A. *et al. Nature* **416,** 610–613 (2002)

One of the mysteries of modern condensed-matter physics is the nature of the pseudogap state of the superconducting cuprates. Kaminski *et al.*[1] claim to have observed signatures of time-reversal symmetry breaking in the pseudogap regime in underdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212). Here we argue that the observed circular dichroism is due to the 5×1 superstructure replica of the electronic bands and therefore cannot be considered as evidence for spontaneous time-reversal symmetry breaking in cuprates.

The main conclusions of Kaminski *et al.* are based on the temperature-dependent circular dichroism observed in a 'mirror' plane of the underdoped Bi2212 thin films. However, Bi2212 samples possess a 5×1 superstructure that breaks reflection symmetry in these planes, as demonstrated by electron diffraction and angle-resolved photoemission (ARPES) experiments (Fig. 1a,b). The 5×1 superstructure is suppressed by doping pristine Bi2212 with lead. We performed ARPES experiments similar to those reported by Kaminski *et al.*[1] on both systems. At room temperature (Fig. 1c), the influence of the superstructure is already obvious: for pristine Bi2212, the dichroic signal is non-zero in the Γ–$(\pi,0)$ plane.

This result can readily be explained. The superstructure results in diffraction replicas of the electronic structure seen in the momentum-distribution map (Fig. 1b) as green and blue dashed curves. Because of the pronounced inequivalence of the matrix elements in the first and second Brillouin zones, the spectral weight of these replicas is always different near the $(\pi,0)$ point. Recording the dichroism as a function of momentum $\mathbf{k}$ along the white double-headed arrow in Fig. 1b, one effectively measures the superposition of the three signals originating from the main band and two non-equivalent diffraction replicas. A systematic investigation of the 5×1 superstructure-free Pb-Bi2212 samples that have a large pseudogap (Fig. 1d) reveals that the dichroism in the mirror plane remains zero within the experimental error bars, independent of temperature (Fig. 1c) and doping[2].

The finite superstructure-induced room-temperature dichroism in the mirror plane must also be present in the thin films, which do exhibit a superstructure signal. The energy-distribution curves (EDCs), which are identical to an accuracy of 0.06% (see Fig. 2e of ref. 1), therefore indicate that they cannot be taken at the $(\pi,0)$ point and that the zero momentum in Fig. 3g of ref. 1 probably does not correspond to the mirror plane. The large uncertainty in locating the actual position in the $\mathbf{k}$-space (not specified by Kaminski *et al.*) is also evident from data shown in their Fig. 3d,h. Presented EDCs for the overdoped sample are claimed to be $\mathbf{k}_f$ EDCs. However, it is known that, at finite temperature at $\mathbf{k}_f$, the spectral function has a peak at the chemical potential and so multiplication by the Fermi function would result in the leading-edge midpoint being located at negative binding energies, which is not the case.

Provided that the zero momentum in Fig. 3g of ref. 1 does not correspond to the $(\pi,0)$ point, the temperature dependence of the dichroism is not surprising. Away from the mirror plane, the dichroism corresponding to the main band is temperature dependent, as can be seen by comparing the slopes of the dichroism in their Fig. 3c (note that the lines shown in Fig. 3c,g of ref. 1 are not always linear fits to the 11 data points, as is evident from the data collected at 150 K) and in Fig. 3d of ref. 2.

The absence of full-range curves[2] in Fig. 3c, g of ref. 1 does not allow the exact location in momentum space from which the presented data are taken to be determined; neither can we determine whether this is

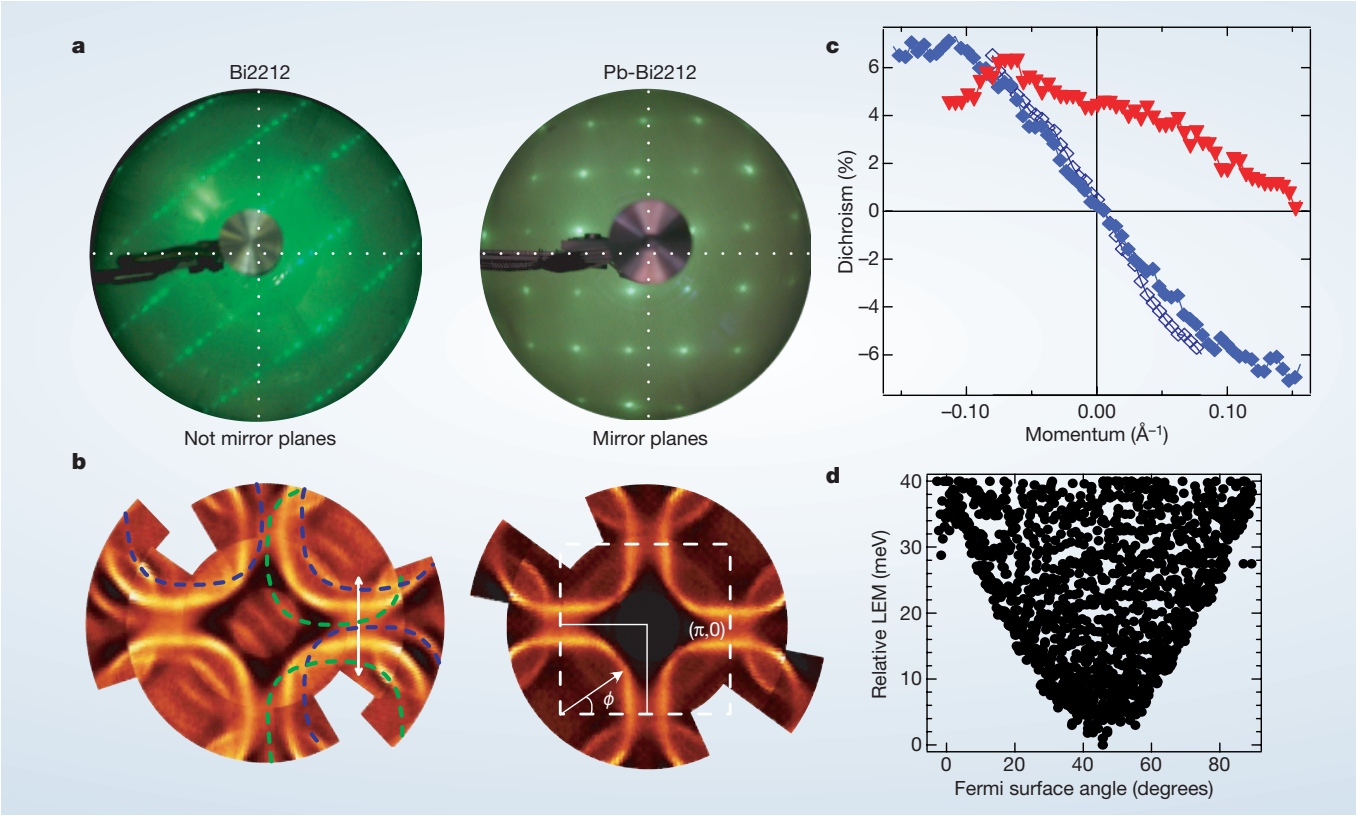

Figure 1 Features of superstructure in superconducting cuprates. **a, b,** Electron diffraction (**a**) and angle-resolved photoemission (**b**), showing angular distributions of the electrons in pristine (left) and Pb-doped (right) Bi2212. White dotted lines, crystallographic planes; green and blue dashed lines, diffraction replicas; white dashed line, first Brillouin zone. **c,** Dichroism near (π, 0) in Bi2212 (red triangles) and Pb-Bi2212 (blue diamonds; filled, 300 K; open, 100 K). **d,** Anisotropic pseudogap in Pb-Bi2212 measured at 120 K as binding energy of the leading-edge midpoints (LEM) for all spectra within the quadrant of the Brillouin zone as a function of Fermi surface angle ϕ (white arrow in **b**, right).

always from the same place. In support of such uncertainty, there is a considerable (about 14%) variation in the slope of the 250 K 'line' in two similarly underdoped samples (see Figs 3g, 4a,b of ref. 1) that cannot be explained by the small difference in doping levels, because comparison with a much more strongly doped sample (Fig. 3c of ref. 1) gives a similar change in slope.

The results presented in Fig. 4a,b of ref. 1 also fit the 'superstructure' scenario: in this, going from the $(\pi,0)$ to the $(0,\pi)$ point (our Fig. 1), the stronger (blue) diffraction replica is now on the other side of the $(0,\pi)$ point and therefore the temperature-induced changes have the opposite sign.

The data of Kaminski *et al.* on the overdoped sample (their Fig. 3c) can be explained by the substantially weaker influence of the diffraction replica in the immediate vicinity of the $(\pi,0)$ point because of the larger size of the Fermi surface (we consider only the bonding sheet, as the antibonding one is strongly suppressed at the photon energies used in ref. 1; Fig. 1b). In addition, the superlattice signal seems to be more sensitive to the temperature in underdoped samples[3] and to vary from sample to sample: Kaminski *et al.* report it to be about 3%, whereas it is about 10% in ref. 4.

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doi:10.1038/nature02931

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Kaminski et al. *reply* — There are two components of the circular dichroism (CD) signal in angle-resolved photoemission (ARPES) measurements. One is always present in crystals, regardless of any time-reversal symmetry considerations. This component, which we refer to as 'geometric', is antisymmetric about any symmetry plane of the crystal, and is therefore zero at that plane. But in underdoped samples of the high-temperature superconductor Bi2212, we find another component, which is non-zero at the symmetry plane below the pseudogap temperature. We attribute that component to time-reversal symmetry breaking. The objections of Borisenko *et al.*[1] comprise three main points: the circular dichroism that we observe at the mirror plane[2] is due to the superstructure of the Bi–O layer; our momentum accuracy is not as we stated; and the absence of dichroism in overdoped samples is due to a weaker influence of the superstructure because of an increased Fermi surface volume compared with underdoped samples.

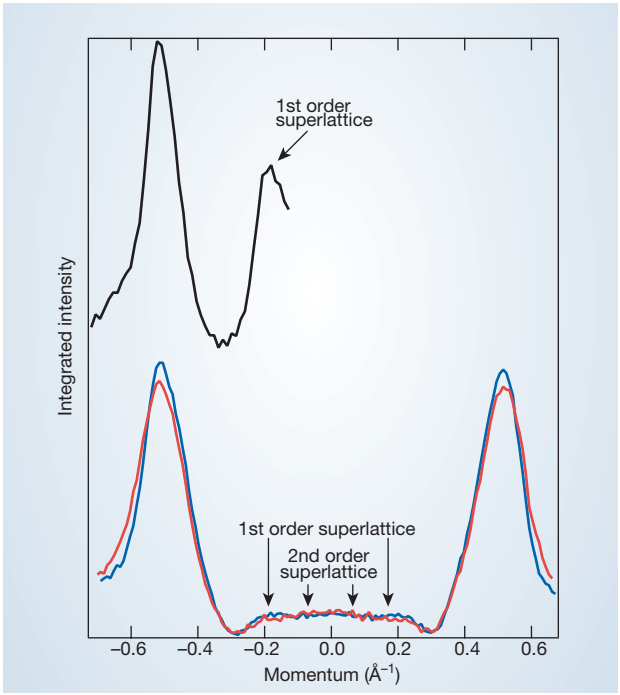

Figure 1 Comparison of the superstructure signal and its effect on the circular dichroism in single-crystal samples and epitaxially grown thin films. The momentum distribution data along the (0,0)–(π,π) direction obtained from a single crystal sample (top black curve) displays a superstructure signal of about 50%. Similar data obtained from epitaxially grown thin films show only a 3% superstructure signal (lower curves: red, 200 K and blue, 50 K).

It is obvious that modulation of the BiO plane breaks reflection symmetry about the Cu–O bond direction in BSCO crystals (that is, those containing Bi, Sr, Ca, Cu, O), but our experiment relies on the fact that the CuO_2 states do not couple to the BiO states, thereby preserving this symmetry[3]. We explicitly test this in Fig. 3f of ref. 2, where we show that there is no dichroism at high temperature at the mirror plane in a sample, but that dichroism does occur below the pseudogap temperature.

The first point of Borisenko *et al.* could only be valid if two conditions were met simultaneously: the superstructure signal would have to be large (about 40%), and either the geometric component of the CD signal or the superstructure signal would have to display significant temperature dependence. The first condition does not hold, as shown by our measurements on epitaxially grown thin films that have a very weak superstructure signal[2,4] (of the order of 3%; Fig. 1). We agree that this signal in single-crystal samples was about 30–50% of the main signal, and we showed earlier[3,5,6] that this was entirely due to the diffraction of the outgoing photoelectron. If the dichroism originates from the superstructure signal, then the 4% dichroism resulting from the 40% superstructure signal in the crystal of Borisenko *et al.*[1] would indicate that our 3% superstructure signal would produce a dichroism of only 0.3% — that is, we would never observe a signal.

The second of the two conditions also fails, as there is strong evidence that the geometric component of the CD does not depend on temperature. The slope of the CD at the mirror plane is due entirely to the antisymmetric component and does not change with temperature (see Fig. 3c,g of ref. 2 and Fig. 4b of ref. 7). More significantly, if the superstructure signal contribution is large, then the dichroism signal would be a nonlinear function of momenta in the vicinity of the $(\pi,0)$ point. Such nonlinear behaviour would be significant, as demonstrated by a simulation of the CD that assumes a 40% level of superstructure signal contamination (results not shown), but this is not seen in our data, which instead resemble the simulation result for a 4% superstructure signal (results not shown). Also, as the superstructure signal does not depend on temperature (Fig. 1), the temperature-dependent CD cannot originate from the superstructure signal.

The second point raised by Borisenko *et al.* is based on a misconception. The midpoint of the leading edge lies at positive binding energies only for a very sharply peaked spectral function. For a broad function, it lies close to the chemical potential. It is clear that the areas beneath the curves in our Fig. 3d (ref. 2) are independent of temperature, which holds only at the Fermi momentum[8,9]. Both our samples and detector were aligned with precision[2].

The third point assumes that the Fermi momentum along the $(\pi,0)$–(π,π) direction changes significantly with doping. Such a change would have to be larger than at least half of the momentum range measured in our experiment (our momentum range was 0.1 Å^{-1}) to produce the alleged effect. This is because in underdoped samples the superstructure would have to be well within our momentum range, and in overdoped samples it would have to lie outside. Other data of Borisenko *et al.*[10] provide the best evidence that such large shifts are not observed experimentally. For example, Fig. 1 of ref. 10 shows that the Fermi momentum for both

overdoped and underdoped samples is similar and equal to 0.15 $Å^{-1}$.

The explanation for our results proposed by Borisenko *et al.* fails to account for both the temperature and doping dependence of the dichroism signal at the mirror plane. Their own data from underdoped samples (Fig. 3c in ref. 7) shows temperature-dependent dichroism at the symmetry plane of about 1%. As those data were obtained from superstructure-signal-free samples, the superstructure cannot be responsible for the observed signal.

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doi:10.1038/nature02932

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