Detection and Implications of a Time-Reversal Breaking State in Underdoped Cuprates

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We present general symmetry considerations on how a time-reversal breaking state may be detected by angle-resolved photoemission using circularly polarized photons as has been proposed earlier. Results of recent experiments utilizing the proposal in underdoped cuprates are analyzed and found to be consistent in their symmetry and magnitude with a theory of the copper oxides. These experiments if correct, together with evidence of a quantum critical point and marginal Fermi-liquid properties near optimum doping, suggest that the essentials of a valid microscopic theory of the phenomena in the cuprates may have been found.

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A major problem in condensed matter physics in the past decade and a half has been the search for a microscopic theory of high temperature superconductivity and associated normal state anomalies [1]. The normal state properties which presage superconductivity imply the inapplicability of the quasiparticle concept and are well described by the marginal Fermi-liquid phenomenology [2]. This prescribes scale-invariant fluctuations governed by a quantum critical point (QCP). A change of symmetry in the normal state with doping is then expected. The crucial questions are the following: Does a state with broken symmetry indeed exist? What is its nature? A microscopic theory based on a general model of the cuprate compounds predicts an elusive phase which breaks time-reversal symmetry due to a spontaneous ordered pattern of currents without changing the translational symmetry of the lattice [3]. The predicted current patterns are shown in Fig. 1. Angle-resolved photoemission experiments using polarized light were suggested to detect such a phase [4]. Here the general symmetry considerations necessary for the experiment and its analysis are derived. These results have been used in recent experimental work [5] to detect a time-reversal breaking (T breaking) phase in underdoped cuprates. The experiments are analyzed here to show that the symmetry of the effect is characteristic of the class of the predicted phases and to rule out some other possibilities.

The proposed experiment [4] looks for dichroism independently for any given $\mathbf{k}$ state by measuring the difference in intensity of angle-resolved photoemission spectra (ARPES) for right and left circular polarized photons [4] in a monodomain sample and analyzing the symmetry of the difference.

For molecules absorbed on surfaces, a geometric effect has been derived [6], which even without T breaking yields intensity which depends on the circular polarization in ARPES experiments. Here we first generalize the geometric effect for the symmetries of a crystal and then derive the conditions necessary to distinguish the geometric effect from the effect due to T breaking.

General results.—Suppose a beam of photons of energy ω shone on a crystal in the direction $\hat{n}$ produces free electons with momentum $\mathbf{p}$ and energy $E_{\mathbf{p}}$ at the detector. Let $|\mathbf{k}\rangle$ denote the states of the crystal. Here $\mathbf{k}$ is the wave vector in the first Brillouin zone. Assuming the momentum of the photons is small compared to $\mathbf{k}$, $\mathbf{p}$, the current $J_{\mathbf{p}}$ is given by

$$J_{\mathbf{p}} = 2\pi e \sum_{\mathbf{k}}^{\prime} f(\epsilon_{\mathbf{k}}) |\langle \mathbf{p}|\mathbf{M}|\mathbf{k}\rangle|^2 \delta(E_{\mathbf{p}} - \epsilon_{\mathbf{k}} + \omega), \quad (1)$$

where the matrix element is given by

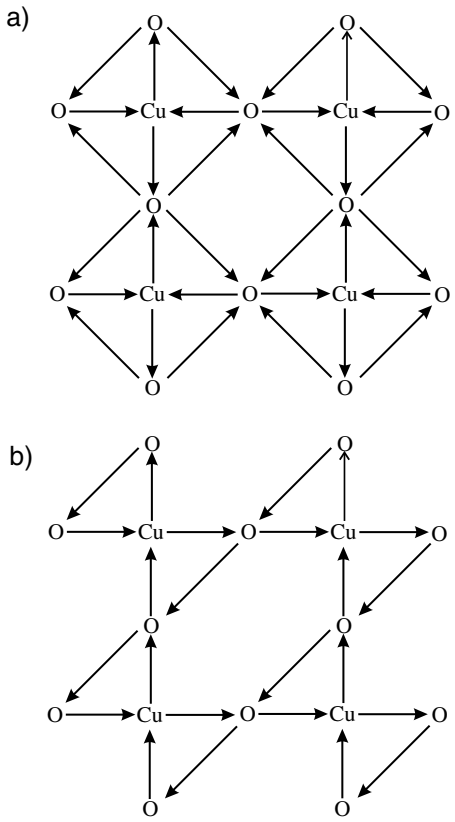

FIG. 1. Current patterns for the predicted T-breaking states that preserves translational invariance.

$$\langle \mathbf{p}|\mathbf{M}|\mathbf{k}\rangle = \frac{-ie}{2mc}\int d\mathbf{r}\Phi_{\mathbf{p}}(\mathbf{r})\mathbf{A}\cdot\nabla\psi_{\mathbf{k}}(\mathbf{r}), \tag{2}$$

and the summation is restricted by momentum conservation between $\mathbf{p}$, $\mathbf{k}$ modulo the reciprocal vectors. Also $\mathbf{A}$ is the vector potential and $\Phi_{\mathbf{p}}(\mathbf{r})$ is the wave function of the outgoing photoelectron of momentum $\mathbf{p}$. We may distinguish the two circular polarizations by $\mathbf{A}_{\ell,\mathbf{r}}$,

$$\mathbf{A}_{\ell,\mathbf{r}} = A_0(-\hat{x}' \pm i\hat{y}'), \tag{3}$$

where $\hat{x}'$ and $\hat{y}'$ are perpendicular to $\hat{n}$, and the two matrix elements by $\mathbf{M}_{\ell,\mathbf{r}}(\mathbf{k},\mathbf{p})$. We will assume that the crystal being studied is two dimensional so that $\mathbf{k}$ refers to the momentum in the x-y plane. Note that, since the momentum of the photon is assumed negligible, $\mathbf{p} = (\mathbf{k} + \mathbf{G})$. So, when $\mathbf{p}$ is in the mirror plane of the crystal, so is $\mathbf{k}$. (The converse is not true.) Let $\hat{m}$ be the set of mirror planes of the crystal normal to the surface of the crystal. For reasons that will be clear shortly, we will consider only the situation in which $\hat{n}$ lies in one of the $\hat{m}$ planes.

We may write in general that

$$\begin{aligned}|\mathbf{p}\rangle &= \alpha_{\mathbf{m}}|\mathbf{p},\mathbf{e}\rangle + \beta_{\mathbf{m}}|\mathbf{p},\mathbf{o}\rangle;\\ |\mathbf{k}\rangle &= \mu_{\mathbf{m}}|\mathbf{k},\mathbf{e}\rangle + \nu_{\mathbf{m}}|\mathbf{k},\mathbf{o}\rangle,\end{aligned} \tag{4}$$

where under reflection $\Re$ about a given m plane,

$$\begin{aligned}\Re_m|\mathbf{p}\rangle &= \alpha_m|\mathbf{p},e\rangle - \beta_m|\mathbf{p},o\rangle;\\ \Re_m|\mathbf{k}\rangle &= \mu_m|\mathbf{k},e\rangle - \nu_m|\mathbf{k},o\rangle.\end{aligned} \tag{5}$$

In Eq. (4), the eigenstates are divided into two parts, of which one has a real space representation even in reflection and the other has a real space representation odd in reflection about the given $\hat{m}$ plane. When T symmetry is preserved, $\nu_m = 0$ if $\mathbf{k}$ lies in the mirror plane.

Because $\hat{n}$ is contained in the mirror plane $\hat{m}$,

$$\Re_m^{-1}(\mathbf{A}_\ell\cdot\nabla)\Re_{\mathbf{m}} = (\mathbf{A}_{\mathbf{r}}\cdot\nabla). \tag{6}$$

We are now finally ready to relate the matrix element for left circular polarization (lcp) with that for right circular polarization (rcp). Using Eq. (6), we can write

$$\mathbf{M}_\ell = \langle\mathbf{p}|\Re^{-1}(\mathbf{A}_{\mathbf{r}}\cdot\nabla)\Re|\mathbf{k}\rangle. \tag{7}$$

Then using Eqs. (5) and (8), $\mathcal{D}_m \equiv |\mathbf{M}_\ell|^2 - |\mathbf{M}_r|^2$:

$$\begin{aligned}\mathcal{D}_m = 4\mathcal{R}(&\alpha_m^*\beta_m|\mu_m|^2\langle\mathbf{p},e|\mathbf{M}_r^*|\mathbf{k},e\rangle\langle\mathbf{k},e|\mathbf{M}_r|\mathbf{p},o\rangle + \beta_m^*\alpha_m|\nu_m|^2\langle\mathbf{p},o|\mathbf{M}_r^*|\mathbf{k},o\rangle\langle\mathbf{k},o|\mathbf{M}_r|\mathbf{p},e\rangle\\ &+ \mu_m\nu_m^*|\alpha_m^2\langle\mathbf{p},e|\mathbf{M}_r^*|\mathbf{k},e\rangle\langle\mathbf{k},o|\mathbf{M}_r|\mathbf{p},e\rangle + \nu_m\mu_m^*|\beta_m|^2\langle\mathbf{p},o|\mathbf{M}_r^*|\mathbf{k},o\rangle\langle\mathbf{k},e|\mathbf{M}_r|\mathbf{p},o\rangle).\end{aligned} \tag{8}$$

The difference in $\mathbf{J}_{\mathbf{p}}$ due to rcp and lcp follows through Eq. (1). In Eq. (8), $\mathcal{R}$ picks up only the real part of its argument. We now separately consider the cases, T symmetry preserved and T symmetry broken.

T symmetry preserved.—As mentioned above, a finite $\mathcal{D}$ exists even in this case due to the geometry of the experiment. For a T-preserving Hamiltonian in a crystal with center of inversion α, β, μ, ν may be taken real. For the geometric effect to be nonzero, it is necessary that either the state $|\mathbf{p}\rangle$ or the state $|\mathbf{k}\rangle$ does not have definite parity under the indicated reflection; this requires that three of the four quantities α, β, μ, ν are nonzero. Since if $\mathbf{p}$ lies in a mirror plane, so does $\mathbf{k}$, the former ensures the latter. Thus the geometric effect is zero if $\mathbf{p}$ lies in the plane $\hat{m}$. Note that we assumed above that $\hat{n}$ lies in the mirror plane $\hat{m}$. If the experimental geometry is such that $\hat{n}$ does not lie in the plane $\hat{m}$, it is possible to show that the geometric effect is present in general even if $\mathbf{p}$ lies in the plane $\hat{m}$.

The induced geometric effect must be distinguished in experiments from the proposed effect due to T breaking. Towards this end, an important result following from Eq. (8) is that the geometric effect is odd with respect to reflection of $\mathbf{p}$ about the $\hat{m}$ plane. Thus, if the outgoing plane wave with momentum $\mathbf{p}$ has a component $\delta\mathbf{p}_{\text{perp}}$ normal to this plane (i.e., when $\beta \neq 0$), the difference of the intensity for (rcp)-ARPES and (lcp)-ARPES changes sign for $\delta\mathbf{p}_{\text{perp}} \rightarrow -\delta\mathbf{p}_{\text{perp}}$.

T symmetry broken.—The specific proposals for T-symmetry breaking in copper-oxide metals that have been considered all lead to a broken reflection symmetry about one or more of the *crystalline* mirror planes. The broken reflection symmetry about a given mirror plane $\bar{m}$ attending a broken T symmetry must be distinguished from that due to a structural or electronic distortion. In the latter cases, diffraction experiments, sensitive to density variations, detect the effect. For broken T-symmetry states proposed, the wave functions may not retain reflection symmetry about some $\bar{m} = \hat{m}$ while the charge density continues to retain it. (Specific examples of this will be given below.) In that case we will continue to call $\bar{m}$ a mirror plane. For example, in the copper-oxide lattice the $x = 0$, $y = 0$, and $x = \pm y$ will continue to be called mirror planes, even though due to broken T symmetry, the wave functions may not be eigenstates of $\Re$ about one or more of these planes.

This has the following consequence in Eq. (8). Consider $\mathbf{p}$ in a mirror plane $\bar{m}$, so that $|\mathbf{p}\rangle = |\mathbf{p}_{\mathbf{e}}\rangle$. Then although $\mathbf{k} = \mathbf{p}$ lies in the plane $\bar{m}$, the wave function $|\mathbf{k}\rangle$ has besides the usual component $|\mathbf{k},\mathbf{e}\rangle$, a component $\theta|\mathbf{k},o\rangle$. It then follows that the third term in Eq. (8) is not zero for $\mathbf{p},\mathbf{k}$ in the plane $\bar{m}$. This is true only for the mirror planes about which reflection symmetry is broken due to T breaking. It then also follows that $\mathcal{D}_{\bar{m}}$ has a part which is even about the mirror planes $\bar{m}$, as may also be checked from Eq. (8).

Polarized ARPES for the proposed state.—We will now consider the special T-breaking states [3] predicted for underdoped cuprates. Such states have been derived for a general Hamiltonian in the space of three orbitals per unit cell for nonlocal interactions above a critical value

depending on the deviation of electronic density x away from half-filling. The phase diagram in the T-x plane, for the proposed T-breaking phase is consistent with the observed "pseudogap" phase in the cuprates [4].

For the case that the difference in energy of the Cu-$d_{x^2-y^2}$ level ϵ_d and the O-$p_{x,y}$ levels $\epsilon_{\mathbf{p}}$ is much less than their hybridization energy t_{pd} and for the direct oxygen-oxygen hopping parameter $t_{pp} \ll t_{pd}$, two sets of *singlet* wave functions for a T-breaking phase preserving translational invariance can be derived in the mean-field approximation. Large local repulsions on both Cu and O sites are assumed, and the nearest neighbor Cu-O interactions $V\sum_{i,a} n_{id}n_{i+a,np}$ are decomposed as a sum of irreducible representations of operators of the form appearing below. The derivation of the first state is fully given in Ref. [4]; that of the other follows exactly the same steps. To the lowest order in $(t_{pp}/t_{pd})\theta$, which is enough to display the symmetries, the ground state of $|\Theta_1\rangle$ is made up of products of $|\mathbf{k}, \theta_1\rangle$:

$$|\mathbf{k}, \theta_1\rangle = (N_k)^{-1}\left[a^+_{\mathbf{k},\theta_1} + 4\frac{t_{pp}}{\epsilon_{\mathbf{k}}} s_x s_y (s_x^2 - s_y^2) n^+_{\mathbf{k}} \right]|0\rangle \quad (9)$$

$$a^+_{\mathbf{k},\theta_1} = \frac{d^+_k}{\sqrt{2}} + \left(\frac{s_x(1 + i\theta_1)\, p^+_{kx} + s_y(1 - i\theta_1)\, p^+_{ky}}{\sqrt{2}s_{xy}} \right),$$

$$n^+_{\mathbf{k}} = (s_y p^+_{kx} - s_x p^+_{ky})/s_{xy},$$

$$\theta_1 = \pm \sum_{\mathbf{k}}{}' [s_x \langle p^+_{x\mathbf{k}} d_{\mathbf{k}}\rangle - s_y \langle p^+_{y,\mathbf{k}} d_{\mathbf{k}}\rangle].$$

The ground state of $|\Theta_2\rangle$ is made up of products of

$$|\mathbf{k}, \theta_2\rangle = (N_k)^{-1}[a^+_{\mathbf{k},\theta_2} + 4\frac{t_{pp}}{\epsilon_{\mathbf{k}}} s_x s_y (s_x^2 - s_y^2) n^+_{\mathbf{k}}]|0\rangle, \quad (10)$$

$$a^+_{\mathbf{k},\theta_2} = \frac{d^+_k}{\sqrt{2}} + \left(\frac{(s_x + i\theta_2 c_x)\, p^+_{kx} + (s_y \pm i\theta_2 c_y)\, p^+_{ky}}{\sqrt{2}s_{xy}} \right),$$

$$\theta_2 = \pm \sum_{\mathbf{k}}{}' [c_x \langle p^+_{x\mathbf{k}} d_{\mathbf{k}}\rangle \pm c_y \langle p^+_{y\mathbf{k}} d_{\mathbf{k}}\rangle].$$

Spin labels have been suppressed. d^+_k, $p^+_{kx,y}$ are, respectively, the creation operators in momentum space for the $d_{x^2-y^2}$ atomic orbital at the Cu-site R_i and the $p_{x,y}$ orbitals at the oxygen site at $(R_i + \frac{a_{x,y}}{2})$, in each cell i. Further $s_{x,y} = \sin(k_{x,y}a/2)$, $c_{x,y} = \cos(k_{x,y}a/2)$, $s^2_{xy} = \sin^2(k_x a/2) + \sin^2(k_y a/2)$, and $\epsilon_{\mathbf{k}} = 2t_{pd}s_{xy}$.

In (9) and (10), the expectation values are determined self-consistently and $(\theta_1, \theta_2) \ll 1$ are assumed. The derived additional terms, proportional to the θ's, break T invariance because the effective Hamiltonians, of which Eqs. (9) and (10) are eigenstates, cannot be made real by any unitary transformation. The ground state currents corresponding to $|\Theta_1\rangle$ and $|\Theta_2\rangle$ are shown in Figs. 1(a) and 1(b), respectively. As may be seen from Eq. (9) or Fig. 1(a), $|\Theta_1\rangle$ retains symmetry about the $x = 0$, $y = 0$ mirror planes, but not about the mirror planes ($\bar{m}_1$:$x = \pm y$). On the other hand as may be seen from Eq. (10) or Fig. 1(b) $|\Theta_{\mathrm{II}}\rangle$ does not retain symmetry about the mirror planes ($\bar{m}_2$:$x = 0$ and $y = 0$). Two of the four possible domains of $|\Theta_2\rangle$ retain reflection symmetry about $x = y$ but not about $x = -y$, while the other two have the opposite behavior. However, $\mathcal{D}$ can be shown to be zero in $|\Theta_2\rangle$ for all of them at both $k_x = \pm k_y$ due to the symmetry of the transfer integral among the two oxygen orbitals in each unit cell.

The symmetry of the states (9) and (10) has the following consequence for $\mathcal{D}$ [7]. The state $|\Theta_1\rangle$ produces an effect in $\mathcal{D}$ of order θ_1 which is even about the $x = \pm y$ mirror planes and zero effect at the $x = 0$, $y = 0$ mirror planes. The state $|\Theta_2\rangle$ produces an effect in $\mathcal{D}$ of order θ_2 which is even about the mirror planes $x = 0$ and $y = 0$. From Eq. (8) it follows that the effect changes sign at these two mirror planes (i.e., if it is positive at one, it is negative at the other) and have maximum absolute magnitude at $(k_x a, k_y a) = (\pm\pi, 0)$. The effect is zero at the mirror planes $x = \pm y$.

Together with the geometric effect, the *effective* mirror planes defined as the plane for $\mathcal{D} = 0$ therefore appear rotated compared to the *crystalline* mirror planes. The rotation is in opposite directions for two mutually orthogonal crystalline mirror planes $\bar{m}$. Further, $\bar{m}$ are the $x = \pm y$ planes for the state $|\Theta_1\rangle$ and the planes $x = 0$ and $y = 0$ for the state $|\Theta_{\mathrm{II}}\rangle$.

Analysis of the experiments.—Recent polarized ARPES experiments [5] to look for the predicted effect [4] give results which are consistent with T breaking in the underdoped phase of the cuprates. In one set of experiments [5], the region of momentum at the edge of the first Brillouin zone near the point $(\pi/a, 0)$ was investigated thoroughly with $\hat{n}$ normal to the Cu-O plane. In the absence of a pseudogap the difference in the current for rcp and lcp ARPES was found to be odd about this point in traveling along the edge of the zone. This serves as a check on the experimental setup. In underdoped samples with pseudogap, a difference, symmetric about this point, was observed below the temperature of appearance of the pseudogap, and none was seen above this temperatures. This result has been seen in several underdoped samples; overdoped samples do not show the effect.

Two other features of the results are especially noteworthy in relation to microscopic theory. An investigation of the Brillouin zone near $(0, \pi/a)$ in a given crystal produced an effect in $\mathcal{D}$ of opposite sign to that around $(\pi/a, 0)$ [5]. In other words, the mirror planes $x = 0$ and $y = 0$ are *effectively* rotated in opposite directions. Therefore, according to the symmmetry considerations above, these experiments are consistent with the state $|\Theta_{\mathrm{II}}\rangle$. Second, the magnitude of the effect is independent of the energy in the range investigated, $\sim$0.5 eV. This is important because in the microscopic theory [3], the magnitude of the effect is essentially uniform over the

entire conduction band. (This is not a Fermi-surface effect). Moreover, the absolute magnitude of the effect, about 5%, is consistent with the expectations.

We also take note of recent μ-sR experiments [8], which observe a slowing down of magnetic fluctuations below the "pseudogap line," consistent with time-reversal breaking, in a variety of cuprate compounds.

We now inquire if any other symmetry breaking can produce the observed effects. It may be seen that lattice distortions of the tetragonal to orthorhombic type, while preserving translational symmetry, do not have the symmetry to produce the observed effect. It may in principle be produced by distortions of the basic two-dimensional unit cell to the shape of a parallelogram, so that the relevant mirror-plane symmetries are lost. Careful investigation of lattice distortions as a function of temperature [5] have not revealed any nor have such distortions been reported elsewhere.

The difference of ARPES intensity for rcp and lcp photons exists for any T-breaking phase, be it due to spin order or orbital order. Antiferromagnetic order at $\mathbf{Q} = (\pi/a, \pi/a)$ would produce a phase breaking reflection symmetry about the $x = \pm y$ planes and is therefore incompatible with the observations. It would produce zero effect for outgoing momenta along the $\bar{m}$ planes $x = 0$, $y = 0$ and maximum at the planes $x = \pm y$. Further, the effect would be zero at the zone edge in these directions. A proposal combining the staggered flux phase [9] with the idea of a quantum critical point near optimum doping has recently been advanced as a possibility for the underdoped compounds with the name "D-density wave" [10]. This phase has the same symmetry as the above antiferromagnetic phase with regard to the ARPES experiment. Moreover, both these phases break translational symmetry so that the Fermi surface consists of four pockets in the π-π directions. This is contrary to the observations by ordinary (linearly polarized) ARPES in the cuprates. More complicated magnetic or structural symmetry breakings can be envisaged producing the observed effect. But they would have to have escaped notice in direct diffraction experiments.

We also note that an anyon state [11] can also be detected by ARPES experiments. For such a state the effective rotation of all the crystalline planes would be in the same direction.

Implications.—The existence of a quantum critical point in the phase diagram [2] of copper oxides near optimum doping suggested that the central feature to be understood in the cuprates is the symmetry of the underdoped state. The ARPES experiments have discovered a state which breaks time-reversal invariance without altering the translational symmetry. Since at least three points are required to define a loop, it is obvious that a state which does not enlarge the unit cell but has ground state currents can only be the property of a model with at least three orbitals per unit cell. Indeed, purely on symmetry grounds (as well as on grounds of its energy independence) the ARPES observations have been identified here to be consistent with a proposed state [3] which is one of the possible ground states of a general copper-oxide model with long range interactions. Approximate solutions of the same model lead to several of the universal features of the phase diagram of the cuprates, including the QCP, the pseudogap phenomena at underdoping, the crossover to a Fermi liquid at overdoping, the vertex for "d-wave" pairing as well as the right energy scale and coupling constant for the high T_c of the cuprates. Heuristic arguments have been presented for the exponents in the phenomenological fluctuation spectra [2] necessary for the marginal Fermi-liquid properties in the normal state near optimum doping. Several properties remain to be understood, especially the reason why no singularity in thermodynamic properties is observed accompanying the time-reversal breaking. Also a better derivation of the phenomenological spectrum [2] is called for. But if the experimental results [5], which ought to be independently confirmed, are correct, the essential ingredients of the theoretical model for the cuprates as well as the principal features of the solution are no longer in doubt.

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