Interpretation of the $La_2CuO_{4+\delta}$ phase diagram

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The phase diagram for a solution of oxygen in La_2CuO_4, including the region of phase stratification, is interpreted on the basis of a nematic spin order parameter. In this interpretation, the small values of the structural changes in the lattice can be explained by the small value of the magnetic-anisotropy energy.

That the $La_2CuO_{4+\delta}$ system is spatially nonuniform and at low temperatures consists of a mixture of metallic and insulating phases was apparently first pointed out in Refs. 1 and 2. Figure 1 is a schematic (T, δ) phase diagram.[3,4] The hatched region corresponds to the interval of the concentration δ in which phase stratification occurs. The symmetry of the OI phase is known reliably—$Cmca(D_{2h}^{18})$—while the OII phase is interpreted either as an orthorhombic face-centered phase[3]—$Fmmm(D_{2h}^{23})$—or one of the monoclinic phases.[4] The existence of a first-order transition below 300 K is also supported by the observation of hysteresis.[5]

The phase stratification upon the dissolution of oxygen is a consequence of the thermodynamics, but a spatial redistribution of the oxygen would be possible at such low temperatures only by virtue of a high mobility of the oxygen.[6] (At this point, we do not have sufficient data for $YBa_2Cu_3O_{6+y}$ solutions.) The growth of nucleating centers of the insulating phase was attributed in Ref. 2 to an attraction of clusters with localized moments as a result of the elastic strain (from the side of the metallic phase). A corresponding mechanism was mentioned in Refs. 5 and 7, in this case for holes introduced in the antiferromagnetic phase; the growth of the clusters results from a decrease in the loss of magnetic energy as carriers come closer together. Below we attempt to relate the entire phase diagram in Fig. 1 to magnetic phenomena. All the characteristic temperatures here correspond to the magnetic scale. In a pure La_2CuO_4, for example, we have $T_N \simeq 250$–320 K and $T_{T\text{-}O} \simeq 500$ K; the exchange integral J is

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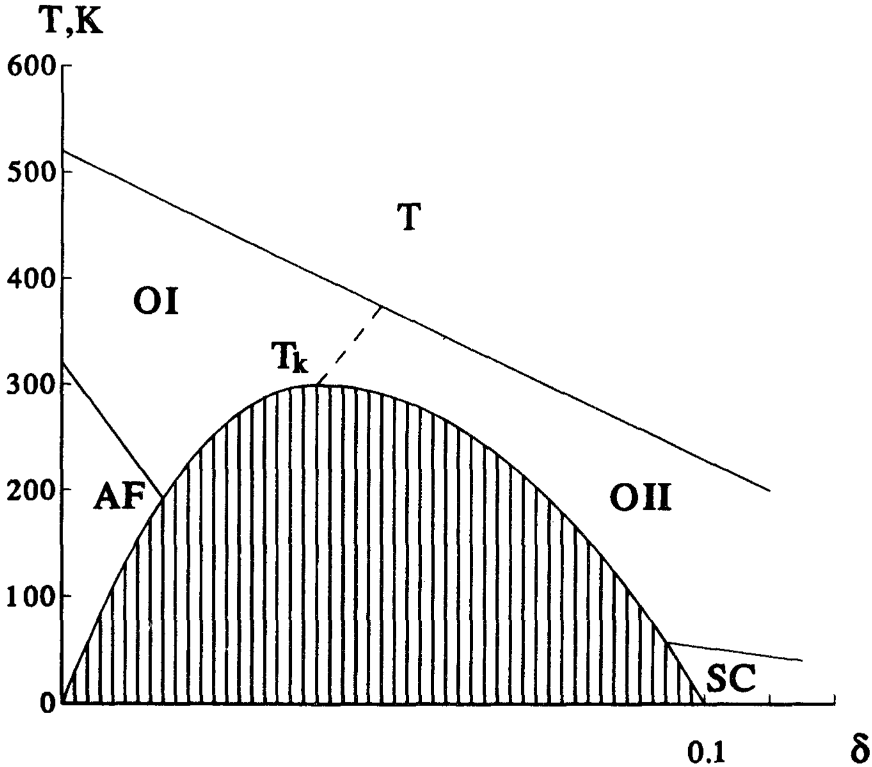

FIG. 1. Phase diagram of $La_2CuO_{4+\delta}$ (Ref. 3). The hatched region is the region of an OI–OII phase stratification.

estimated to be $J \simeq 0.1$ eV (see the review in Ref. 8, for example); and the critical point in Fig. 1 is at $T_K \simeq 300$ K (Refs. 3 and 5). The presence of an antiferromagnetic phase in La_2CuO_4 proves that there is a local moment associated with the copper ion Cu^{2+} (d^9). The phase diagram is concentrated at comparatively low values $\delta \leqslant 0.1$. It is thus not likely that the local moment would disappear completely outside the antiferromagnetic region. In order to relate the transitions in Fig. 1 to magnetic phenomena, we assume that where there is no antiferromagnetic ordering there can be an ordering which is invariant under $t \to -t$: a spin nematic state manifested in the existence of nonzero anisotropic correlation functions $\langle S_\alpha(1) S_\beta(2) \rangle \neq \delta_{\alpha\beta} F(1-2)$.

The T–O structural transition in La_2CuO_4 is usually explained in terms of phonon modes and rotations of long oxygen octahedra. We find the exceedingly small changes in the lattice structure unusual: $2(a-b)/(a+b) \simeq 10^{-2}$–$10^{-3}$ in the orthogonal phase, with an octahedron rotation angle $\phi_0 \sim 5 \times 10^{-2}$ rad. Below we examine the implications for the phase diagram in Fig. 1 which follow from the suggestion that a nematic spin order parameter is predominant in the $La_2CuO_{4+\delta}$ system and that the structural changes result from slight relativistic magnetoelastic interactions $(\sim v^2/c^2)$.

References are cited in Ref. 9, and it is stated that—in contrast with the arguments presented in those references— the source of the quadrupole order of the spins at the various atoms might be a long-range antiferromagnetic interaction (or "frustration"). The compound La_2CuO_4 is a layered compound. The antiferromagnetic 3D transition is thus preceded by a temperature interval of 2D fluctuations.[8] We are going to ignore that circumstance, assuming that the nematic transition—if it occurs—also arises from interplanar interactions.

The exchange interaction is primarily responsible for the spin order. We will classify[10] the states in accordance with representations of the exchange group $S(3)\times G$, where $S(3)$ contains only spin rotations and reversal (i.e., $t\to -t$), while G is the space group of the paramagnetic phase. At high temperatures, La_2CuO_4 has a tetragonal symmetry (the group $I4/mmm\text{–}D_{4h}^{17}$). Two types of binary spin correlation functions are possible (for $S=1/2$):

$$< S_\alpha(1)S_\beta(2) >= T_{\alpha\beta}\phi(r_1,r_2), \quad (1)$$

where $T_{\alpha\beta}=T_{\beta\alpha}$ and $T_{\alpha\alpha}=0$ (this is the case of an ordinary nematic), and

$$< S_\alpha(1)S_\beta(2) >= e_{\alpha\beta\gamma}P_\gamma(r_1,r_2), \quad (2)$$

the case of a "p-nematic," according to Ref. 11. The functions $\phi(r_1,r_2)$ and $P_\gamma(r_1,r_2)$ usually transform under one-dimensional representations of the space group.

It is necessary to restore the form of the spin expectation values in (1) and (2) under the assumption that the structural distortions below $T_{T\text{–}O}$ result from magnetoelastic interactions. In tetragonal terms (the x and y axes run along the sides of a CuO_2 square), the body-centered lattice doubles below $T_{T\text{–}O}$ (Ref. 12, for example). The deformation of the octahedra is conveniently characterized by the rotation angle $\delta\vec{\Omega}(r_n)$. In the orthorhombic axes $(x'y')$, rotated 45°, we have

$$\delta\Omega_{y'}(r_n) = \tilde{w}_{y'}\exp(i\vec{Q}_0\vec{r}_n)\ , \quad (3)$$

where the vector Q_0 is $(\pi/a,\pi/a,0)$ in tetragonal axes or $(\sqrt{2}\pi/a)(1,0,0)$ in the axes $(x'y')$. The vector $\tilde{w}_{y'}$ correspondingly transforms under an even representation y' (i.e., as a product zx') of the subgroup of the vector $\vec{Q}_0$. Since $\vec{P}$ in (2) changes sign under the substitution $\vec{r}_1\to\vec{r}_2$, we are left with a parameter in the form in (1). As a basis function with a broken tetragonal symmetry we adopt

$$< S_\alpha(1)S_\beta(2) >= T_{\alpha\beta}\cos\left(\frac{\pi\vec{Q}_0\vec{R}}{2}\right)\phi_n(\vec{r}), \quad (3')$$

where $\vec{R}=\vec{r}_1+\vec{r}_2$, $\vec{r}=\vec{r}_1-\vec{r}_2$, and the subscript n on $\phi_n(\vec{r})$ specifies one of the possible representations. In this paper we assume that ϕ_n corresponds to a unique representation. Strictly speaking, the general form of the tensor $T_{\alpha\beta}$ is biaxial (with eigenvalues λ_1, λ_2 and $-\lambda_1$, $-\lambda_2$). Its axes are fixed by the magnetic anisotropy. According to (3), only the invariant $\tilde{w}_{y'}\cdot T_{zx'}$ is nonzero. For the tetragonal phase we introduce (in the standard way) two anisotropy constants, K_1T_{zz} and $K_2T_{xy}^2$, which depend on T and δ.

Let us consider two examples. We assume $T_{\alpha\beta}=\frac{1}{2}(a_\alpha b_\beta + a_\beta b_\alpha)$, where the vectors $\vec{a}$ and $\vec{b}$ are perpendicular: $T_{\alpha\alpha} \equiv (\vec{a}\vec{b}) = 0$. We assume $K_2 > 0$; then $\vec{a}$ and $\vec{b}$ lie in the (zx') plane, along the z and x' axes; i.e., we have $T_{zx'} \neq 0$. Let us assume that K_2 changes sign on the line $K_2(T,\delta) = 0$. However, the direction in which the octahedra rotate changes abruptly by 45°. [A similar first-order transition has been observed[13] for $(La_{1-x}Ba_x)_2CuO_{4-\delta}$ in the interval $0.035 < x < 0.1$.]

The other example is a uniaxial spin nematic,[11] with $T_{\alpha\beta} = n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}$. We assume that the fourth-order magnetic anisotropy is such that the vector $\vec{n}$ lies in the (zx') plane. The anisotropy energy $U_{\rm anis} = \tilde{K}_1 \sin^2\theta + \frac{1}{2}\tilde{K}_2 \sin^4\theta$ has a minimum at $\sin^2\theta_0 = -\tilde{K}_1/\tilde{K}_2$ if $\tilde{K}_2 < 0$, $\tilde{K}_1 > 0$ ($\tilde{K}_1$ is of the easy-axis type). Here are the two possibilities for lines of transitions: A phase with $\theta_0 \neq 0$ converts into a phase with $\theta_0 = 0$ on the line $\tilde{K}_1(T,\delta) = 0$. This distortion of the octahedra disappears; we have $T_{zx'} = 0$; and the structure is tetragonal. The second possibility is more interesting: The vector $\vec{n}$ rotates to a position along the x' axis: $T_{zx'}$ is again zero. The tilting of the octahedra is therefore again zero, but a face-centered orthogonal phase, $Fmmm(D_{2h}^{23})$, arises, as we will now see. The line of second-order transitions, $\tilde{K}_1(T,\delta) + \tilde{K}_2(T,\delta) = 0$, may transform continuously into a line of first-order transitions at the point T_K (Fig. 1).

The last point which requires some explanation is an orthorhombic deformation at $\vec{K} = 0$. The order parameter in (3') in second order (near T_c) generates a term $T_{\alpha\nu}T_{\nu\beta} \propto (n_\alpha n_\beta + \frac{1}{3}\delta_{\alpha\beta})$ at $\vec{K} = 0$ even in the exchange approximation. The relativistic terms then give rise to magnetoelastic interactions with a strain tensor $\epsilon_{\alpha\beta}$. In the phase with $\theta_0 \neq 0$, for example, there is a term $\epsilon_{x'x'} T^2_{x'z'}$. The quantity $(a-b)/(a+b)$ is therefore proportional to the square of the order parameter, (3'), and is small ($\sim v^2/c^2$). For the leading parameter in (3) we would again find the elastic strain proportional to the square of the order parameter,[12] but the elastic strain would be smaller by about two orders of magnitude, because $\delta\Omega$ itself is small.

The assumption of a nematic spin order in La_2CuO_4 is thus consistent with Fig. 1. Moreover, this assumption does not contradict antiferromagnetic correlations outside the region of the antiferromagnetic state: The functions $\phi_n(\vec{r})$ in (3') may fall off slowly with distance and may depend on the temperature. The observation of a "softening" of the phonon mode, $\omega(Q_0)$, at $T_{T\text{-}O}$ in Ref. 12 is a more complicated question. On the one hand, in the exchange approximation an anisotropic nematic has low-lying degrees of freedom[10,11] corresponding to free rotations in the $S(3)$ groups; i.e., there are soft modes at point X. On the other hand, it is not clear at this point whether they are observed in inelastic neutron scattering in Ref. 12: The linkup of the spin rotations with the lattice vibrations is a consequence of relativistic effects and is weak. Both a theoretical analysis and more detailed experiments are necessary here. In principle, polarized-neutron experiments might provide information about the anisotropy of the spin correlations. Other possibilities would be to analyze the temperature dependence of the anisotropy of the magnetic susceptibility and NMR data. Finally, there is the possibility of a fairly direct experiment: a study of the effect of a sufficiently strong magnetic field on the lattice symmetry (a "spin–flip" transition outside the antiferromagnetic region).

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