Second harmonic of the longitudinal nonlinear response of slightly doped $La_2CuO_{4+\delta}$ single crystals and new features of the phase separation

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The first results of a study of the longitudinal nonlinear response of three slightly doped $La_2CuO_{4+\delta}$ single crystals at excess-oxygen concentrations corresponding to the region of phase separation are reported. Features of the response are linked with the formation of domains having properties characteristic of an antiferromagnet with a weak ferromagnetism. Estimates are found for their dimensions: $\xi_{\parallel} \sim 4.5 \times 10^3$ Å in the CuO_2 plane and $\xi_{\perp} \geqslant 260$ Å in the orthogonal direction.

One of the most interesting aspects of the superconductivity, antiferromagnetism, and phase separation in $La_2CuO_{4+\delta}$ is the interrelation among these phenomena. The stoichiometric insulator La_2CuO_4 goes into an antiferromagnetic state at $T_N \approx 325$ K (Ref. 1). Even slight doping strongly affects the magnetic properties of this compound, reducing T_N sharply.[1,2] In samples which are not doped too heavily, a phase separation occurs at a certain temperature T_{ps}. One of the regions resulting from this separation is a region of approximately stoichiometric La_2CuO_4, and the other is an O_2-rich conducting phase. The latter phase is responsible for the superconducting properties, which are manifested at $T \leqslant 40$ K (Refs. 3–5). Phase separation is characteristic of many of the superconducting cuprates, and the mechanisms for it and the properties of the resulting phases are being studied actively.[6]

Recent results on ceramic $La_2CuO_{4+\delta}$ samples with $T_N \simeq T_{ps}$ ($\delta \sim 5 \times 10^{-3}$) demonstrate that moderately doped samples are the most interesting.[7,8] Only scant information is available on the magnetic properties of such compounds. It is usually possible to measure only the static susceptibility χ, which, aside from the shift of T_N, is not greatly different from χ of a stoichiometric sample. The sensitivity of χ to phase separation, which was exploited in Refs. 7 and 8, is a consequence of the nonequilibrium nature of the sample, which is itself a result of the rapid cooling. No new magnetic properties associated with phase separation have been observed. There are no data on the dynamic uniformity of χ—such data would be of importance for clarifying such properties—primarily because there is no ESR signal.[9]

In this letter we are reporting the results of a first study of the longitudinal nonlinear response of three lightly doped $La_2CuO_{4+\delta}$ single crystals. As we will see, the onset and the features of this response are directly related to new magnetic properties of the antiferromagnet which arise in the course of the phase separation.

The single crystals ($\sim 2\times 2\times 3$ mm) were grown by the standard method, described in Ref. 10. All the crystals were taken from a single lot.

Since the magnetic-ordering temperature T_N is a known function of δ (Ref. 11), it was used to characterize the amount of excess oxygen in the crystals. To determine T_{ps}, we used data on the correlation between T_{ps} and T_N (Ref. 5). The value of T_N was found from the temperature dependence of χ. We found $T_{N1}=222$ K $<T_{ps}$ for sample N1 ($m_1=91$ mg) and $T_{N2}=272$ K $>T_{ps}\approx 200$ K for N2 ($m_2=86$ mg). We were unable to see an ESR signal in these samples at temperatures up to $T=350$ K.

The longitudinal dynamic response was studied by a method like that described in Ref. 12, but the sensitivity was improved by two orders of magnitude.[13] The test samples were immersed in a static magnetic field and a sinusoidally varying magnetic field, which were parallel to each other: $H(t)=H+h\sin 2\pi ft$ ($f=16$ MHz, $h=45$ Oe). The phase components of the second harmonic of the magnetization, $M_2^{\cos}=\mathrm{Re}(M_2^{\parallel})$ and $M_2^{\sin}=\mathrm{Im}(M_2^{\parallel})$, were measured as functions of the static magnetic field at various sample temperatures. Care was taken to satisfy the condition $M_2\propto h^2$. The experimental apparatus, the method for distinguishing the phase components of M_2 from the longitudinal response, and the method for measuring the sample temperature (the error here was less than 0.2 K) are all described in Refs. 12–14. Experiments were carried out over the temperature range 140–300 K. The sample was held at each temperature for 300 s before the measurement was taken.

Figure 1 shows several signals from sample N3 ($T_N=243$ K $\simeq T_{ps}$) near T_N for the case in which the magnetic field is directed perpendicular to the CuO_2 planes. We will characterize experimental curves of this sort by means of (a) the amplitudes of the curves at the points of the extrema and (b) the positions of these extrema in the static magnetic field (the H position; Fig. 1). Figures 2 and 3 show these properties as a function of the temperature for sample N3, which exhibited the largest M_2 signal. The signal from sample N1 ($T_N=222$ K $<T_{ps}$) had the same qualitative features.

The experimental data can be summarized as follows:

1. The M_2 signal is strongly anisotropic for all the test samples. It is at a maximum when H is perpendicular to the CuO_2 planes. In the case $H\|CuO_2$ planes, the signals are smaller by at least an order of magnitude.

2. For all the test samples, the M_2 signals are observed only in the phase-separation temperature region. For samples N1 and N3, for which T_N is in the phase-separation region, the signals are much stronger than that for sample N2, for which T_N lies above this region. We restrict the discussion below to the data on samples N1 and N3.

3. Near T_N, the curve of $\mathrm{Re}\,M_2(\omega, H)$ versus H has two extrema (a minimum and a maximum), while the curve of $\mathrm{Im}\,M_2(\omega, H)$ has only one (a maximum). All the extrema are observed in a very weak static field: $H_{m1}^{\cos}\simeq 5$ Oe and $H_{m2}^{\cos}\simeq 40$ Oe in $M_2^{\cos}$ and $H_m^{\sin}\simeq 20$ Oe in $M_2^{\sin}$. The first extremum in $M_2^{\cos}$ disappears above T_N (Figs. 1–3).

4. The amplitudes of the extrema (in the case of $M_2^{\cos}$, we mean the amplitude of

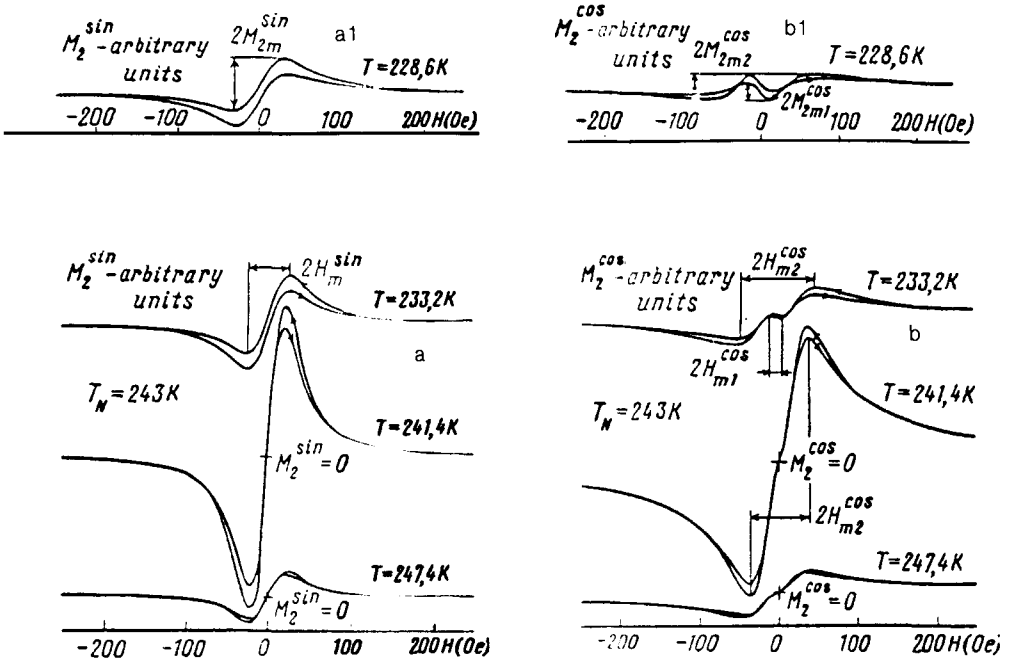

FIG. 1. Amplitudes of the phase components Re $M_2=M_2^{cos}$ and Im $M_2=M_2^{sin}$ as a function of the magnetic field H for $La_2CuO_{4+\delta}$ sample N3 ($T_N=243$ K $\simeq T_{ps}$) near T_N. The scales for parts a1 and b1 of this figure are in the ratio 2.5:1 (the scale is larger than for parts a and b).

only the second extremum) have a strong T dependence, going through a maximum at $T\simeq T_N$ in both phase components.

5. The field positions of the extrema do not depend on the temperature between $T\simeq T_N+10$ K and $T\simeq T_N-5$ K. Outside this region, the H positions of the extrema shift toward stronger fields.

6. A field hysteresis is observed in the signal at $T\leqslant T_N$ (Fig. 1).

7. The amplitudes of the two phase components are of the same order of magnitude.

The M_2 signal is quite reproducible in all cases.

We will limit the analysis to M_2 in the critical paramagnetic vicinity of T_N. The features in the response near T_N (the independence of the H positions of the extrema from increases in their amplitudes) imply an increase in the volume of that phase of the sample which contributes the signal, without a change in its critical properties, as τ decreases. This behavior is seen in regions with a size smaller than the correlation length.[15] The basic task here is to determine the nature of the fragmentation in terms of oxygen in the course of the phase separation, which may be responsible for the anisotropic nonlinear response in an extremely weak field.

The longitudinal dynamic response of a magnetic material is known to be gov-

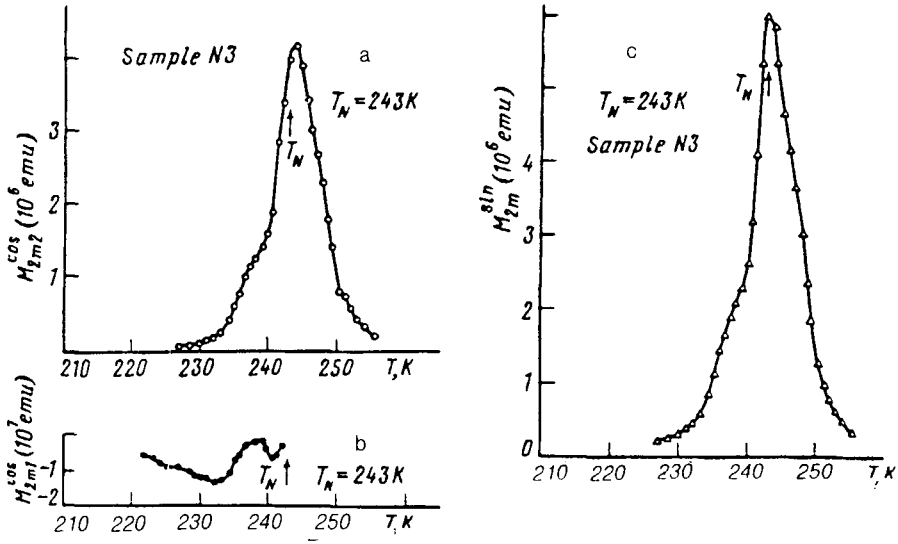

FIG. 2. Amplitudes of the extrema of $\mathrm{Re}\, M_2 = M_2^{\cos}$ and $\mathrm{Im}\, M_2 = M_2^{\sin}$ versus the temperature for $La_2CuO_{4+\delta}$ sample N3 (T_N=243 K).

erned by anisotropic interactions which disrupt the conservation of the projection of M onto H; this projection is conserved in the exchange approximation. These forces are small in La_2CuO_4 and can be dealt with by perturbation theory over a broad temperature range, except in the immediate vicinity of T_N (Ref. 16). In this case, there is an explicit expression for the susceptibility[14] $\chi_2(\omega)$, which determines M_2 under conditions $M_2 \sim h^2$: $M_2(t) = -h^2 \mathrm{Re}\{\chi_2(\omega)\exp(-2i\omega t)\}$. This expression is a sum of two contributions, corresponding to two general factors which are responsible

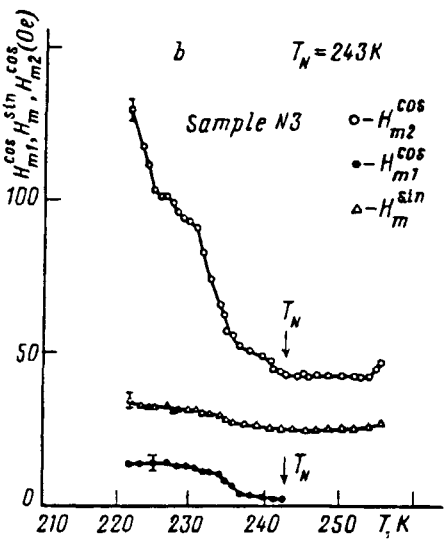

FIG. 3. H positions of the extrema of $\mathrm{Re}\, M_2 = M_2^{\cos}$ and $\mathrm{Im}\, M_2 = M_2^{\sin}$ versus the temperature for $La_2CuO_{4+\delta}$ sample N3 (T_N=243 K). ○—$H_{m2}^{\cos}$; □—$H_{m1}^{\cos}$; △—$H_m^{\sin}$.

for the behavior of M_2, namely the nonlinearity of $M(H)$ and the effect of H on relaxation processes. However, estimates carried out for the CuO_2 plane (the interplanar coupling is weak) show that the experimental data are at odds with this result.[17] The onset of the signal is thus associated with a substantial perturbation of the system by weak forces.

When there is a pronounced deviation from exchange isotropy, the spin diffusion, which is the cause of the purely dynamic nonlinear response in a weak field,[14] is ineffective. On the other hand, a Dzyaloshinskiĭ–Mori (DM) interaction occurs in the CuO_2 plane. This interaction couples M with the antiferromagnetism vector. Since this coupling leads to a nonlinearity of $M(H)$ near T_N, we would expect that M_2 would be due to this factor.

In the samples with excess oxygen, there is only a limited increase in the 2D correlation length ξ in the limit $T \to 0$. In a crystal with a uniform distribution of the additional oxygen we would have[18]

$$\xi(\delta, T) = [\xi^{-1}(\delta, 0) + \xi^{-1}(0, T)]^{-1}, \tag{1}$$

where $\xi(\delta, 0)$ is determined by the excess O_2 (by holes), and $\xi(0, T)$ is the 2D Heisenberg ξ. For the test sample which undergoes phase separation at $T = T_N \simeq T_{ps} \approx 250$ K, we use the results $\xi(0, T) = 2 \times 10^3$ Å and $\xi(\delta, 0) \approx 300$ Å for the crystal with $T_N = 190$ K (Ref. 18) and find $\xi(\delta, T) \simeq \xi(\delta, 0)$. This result means that ξ can increase to 2×10^3 Å in stoichiometric domains. Let us examine the nonlinear behavior of the CuO_2 plane with this circumstance in mind. To describe this behavior we use a generalization of the isotropic Hamiltonian[19] which incorporates anisotropic forces in the standard way:

$$H = \int d^2x \left\{ \frac{1}{2} \rho_s |\nabla \cdot \mathbf{l}|^2 + J((\alpha_{xy}/a^2) l_b^2 + 4\alpha_{DM}[\mathbf{m} \times \mathbf{l}]_a) + \frac{1}{2} \chi_0^{-1} \mathbf{m}^2 - \mathbf{m} \cdot \mathbf{H} \right\}. \tag{2}$$

Here ρ_s is the spin stiffness, $\mathbf{l}$ is the local sublattice magnetization ($|\mathbf{l}| = 1$); $\mathbf{m}$ is the local magnetization; α_{xy} and α_{DM} describe the easy-plane anisotropy and the DM interaction; J is an exchange integral; χ_0 is the susceptibility; and a is a lattice constant ($g\mu = 1$). For La_2CuO_4 we have $J \simeq 135$ meV and $2\pi\rho_s = 140$–150 meV (Ref. 18). The anisotropic constants are known[18] for the initial spin Hamiltonian: $\alpha_{xy}^{(0)} = 1.5 \times 10^{-4}$ and $\alpha_{DM}^{(0)} = 7.5 \times 10^{-3}$. In the estimates below we will use values which correspond to the classical transition to a continuous limit in this part of H: $\alpha_i = zS^2 \alpha_i^{(0)} \approx \alpha_i^{(0)}$, where $z = 4$ is the number of nearest neighbors, and $S = 1/2$ ($\mathbf{m}$ has not been normalized to S).

An integration over m of the distribution function corresponding to H yields an effective Hamiltonian for $\mathbf{l}$. In the case $\mathbf{H} \| \mathbf{b}$, using[19] $\chi_0^{-1} = 2Jza^2$, we find

$$H_l = \int d^2x \left\{ \frac{1}{2} \rho_s |\nabla \cdot \mathbf{l}|^2 + a^{-2} J(\tilde{\alpha}_{xy} l_b^2 - \alpha_c l_c^2) + a^{-2} \tilde{H} l_c / 2 \right\}, \tag{3}$$

where $\alpha_c=(\alpha_{DM})^2=5.8\times10^{-5}$, $\tilde{\alpha}_{xy}=\alpha_{xy}-\alpha_c=9.4\times10^{-5}$ and $\tilde{H}=\alpha_{DM}H$. The easy-axis anisotropy ($\alpha_c l_c^2$) and the coupling of l_c with H are consequences of the DM interaction. Because of the relationship between M and l which follows from (2) in the uniform limit,

$$M_b=(\chi_0 H-4J_{DM}\chi_0 l_c)a^{-2}, \tag{4}$$

the nonlinearity of $l_c(H)$ leads to a nonlinearity of $M_b(H)$. With increasing ξ, the plane undergoes a crossover from a 2D Heisenberg plane to the XY regime at $(\xi_{xy}/a)^{-2}\sim\tilde{\alpha}_{xy}2J/\rho_s\approx10\times10^{-4}$ or $\xi_{xy}\approx120$ Å ($a\simeq3.8$ Å). Since we have $\alpha_c\simeq\tilde{\alpha}_{xy}$, the XY crossover is accompanied by the simultaneous onset of an Ising regime. We note that $(\xi_{xy}/a)^{-2}$ is close to the value 6.5×10^{-4}, which was found in Ref. 18 from data on neutron scattering; i.e., the values found above for the anisotropic constants are fairly reliable.

Let us estimate the effect of H. For definiteness, we adopt $H_{m2}^{cos}\simeq40$ Oe as a scale value of the nonlinearity for Re $M_2(\omega)\propto$ Re $\chi_2(\omega)$ (Figs. 1 and 2). An estimate of the corresponding value of ξ from the relation[20] $(\xi/a)^{-2}\sim2\tilde{H}/\rho_s$ yields $\xi_H\approx7.5\times10^3$ Å. This value corresponds to a point deep in the Ising regime [the same result is found from an estimate $(\xi/a)^{-2}\sim H/T_N$ for a 2D Ising magnetic material with $T_N\approx250$ K]. The nonlinear behavior of the plane is extremely anisotropic. In the case $H\perp b$, the H_c component of the field affects l_b. However, ξ is limited along b by ξ_{xy}, so there is an anomalously high field, $\sim(\xi_{xy}/\xi_H)^2\times40$ Oe$\simeq40$ kOe, corresponding to the nonlinear regime.

A plane can be assumed to be isolated if $\xi\leqslant\xi_{3D}=a(T/J_\perp)^{1/2}$, where $J_\perp\simeq2$ meV (Ref. 21) is the interplanar coupling. Since we have $\xi_{3D}\approx110$ Å$\ll\xi_H$ at $T=250$ K, we need to take 3D effects into account in order to explain the nonlinear behavior.

Because of the purely antiferromagnetic 3D order of the samples with a uniform distribution of the excess O2, the field effect, which is characteristic of an isolated plane, is limited to the value $\tilde{H}\sim T(\xi_{3D}/a)^{-2}=J_\perp$ ($H\sim30$ kOe). This circumstance explains why there is no signal near T_N in the sample with $T_N=272$ K. The situation changes sharply in the case of nonequivalent planes. The O_2 concentration in the regions which form during the phase separation,[22] $\delta\approx0.1$, is far higher than the average value in our crystals, $\delta\approx5\times10^{-3}$. A typical domain can thus be represented as a 3D stoichiometric fragment in which rare inclusions of oxygen-rich, approximately planar regions alternate along the b axis.[22] These regions have a small 2D value $\xi_0\sim60$ Å (this estimate was based on the average distance between the excess oxygen atoms). The change in the critical behavior in the course of a fragmentation of this sort can be understood by looking at the example of a system consisting of periodically arranged fragments containing a large number $N(\sim10)$ of "pure" planes and one "defective" plane. As is demonstrated by the incorporation of $J_\perp$ in the molecular-field approximation, a disruption of the equivalence of the planes makes the quantity $L_c=\Sigma_i l_{ic}$ critical; i.e. the system becomes ordered with $\langle L_c\rangle\neq0$ and it exhibits a weak ferromagnetism, since we have $\langle M_b\rangle\propto\langle L_c\rangle$ [see (4)]. The field H remains the conjugate of the order parameter. In a first approximation, the susceptibility corresponding to L_c breaks up into two parts. Under the condition $\xi^2\gg\xi_0^2$, the critical part can be represented somewhat crudely by $\chi^*\sim A[T(a/\xi)^2-J_\perp]^{-1}$. Its amplitude is

small, $A \sim N^{-1}$. The noncritical part is modified slightly by the defective plane. The nonlinearity of the $L_c(H)$ dependence and thus that of the $M_b(H)$ dependence is associated with the critical part. The transition into this regime along the τ scale in the 3D case is found from the usual condition for a 3D ferromagnet:[20] $\tilde{H} \sim CJ_\perp \tau_H^{5/3}$, where the dimensional factor $J_\perp$ is reconstructed through a joining with the 2D regime. If the coefficient C is known, we can find estimates for the correlation lengths which we need in the plane, $\xi_H^{\parallel}$, and along the b axis, $\xi_H^{\perp}$, from Ref. 23: $\xi_H^{\parallel} \sim \xi_{3D}\tau_H^{-2/3}$ and $\xi_H^{\perp} \sim a_\perp \tau_H^{-2/3}$ ($a_\perp = 6.5$ Å is the interplanar distance). Let us estimate C. Since we have $\chi^* \sim (A/J_\perp)\tau^{-4/3}$ in the 3D regime, we would not expect C to be greatly different from $A^{-1} \sim N$. As an estimate of N we can use the ratio of the concentrations of excess O_2 in the oxygen-rich phase to the average density before separation,[22] i.e., $N \simeq 10$–20. Using $H_m^{\cos} \simeq 40$ Oe and $C \simeq 15$, we find $\xi_H^{\parallel} \sim 40\xi_{3D} \approx 4.5 \times 10^3$ Å and $\xi_H^{\perp} \sim 40a_\perp \approx 260$ Å. We have determined $\xi_H^{\parallel,\perp}$ for an unbounded sample. The critical properties of a fragment of a sample will not depend on τ as τ decreases further, if its size in the plane is on the order of $\xi_H^{\parallel}$. Its transverse scale dimension is no less than $\xi_H^{\perp}$ here. We cannot fix the scale along b and leave it free in a plane, since ξ depends strongly on τ in the 2D anisotropic regime.

The nonlinear contribution of these regions to M exists in weak fields. In strong fields, their susceptibility differs only slightly from χ for a stoichiometric fragment. In measurements of M in such fields, we thus observe only the behavior which is the standard behavior for $La_2CuO_{4+\delta}$. The pronounced anisotropy of the signal in the 3D regime is due to the XY anisotropy of the plane, mentioned above.

This picture also yields a natural explanation of the onset of a significant field hysteresis in the signal at $T < T_N$ (Fig. 1). Specifically, this hysteresis is a consequence of the onset of a weak, spontaneous magnetization along the b axis.

In summary, approximately stoichiometric domains with a longitudinal dimension $\xi_H^{\parallel}$ form in the course of the phase separation. These domains contain $\xi_H^{\perp}/Na_\perp \sim 2-3$ oxygen-rich layers over a transverse scale length $\xi_H^{\perp}$. If we assume that the redistribution of excess oxygen occurs primarily within a domain, then uniformly distributed O_2 simply clusters into a small number of layers. An important element of the phase separation is the rigidly fixed longitudinal dimension of a domain of the new phase; this feature is not a matter of chance, since the value of $H_{m2}^{\cos}$ in the sample with $T_N = 222$ K is the same as that in the sample with $T_N = 243$ K.

The features of the response below T_N will be discussed in a separate paper.

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