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Phase separation and weak ferromagnetism in lightly-oxygen-doped La_2CuO_{4+x} single crystals in low magnetic fields

A. A. Zakharov*
Department of Synchrotron Radiation Research, Institute of Physics, Box 118, S-22100, Lund, Sweden

A. A. Nikonov and O. E. Parfionov
Russian Scientific Center ''Kurchatov Institute,'' 123182, Moscow, Russia

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Ferromagnetic regions formed in lightly-oxygen-doped La_2CuO_{4+x} single crystals have been detected by measuring magnetic susceptibility in low (<50 Oe) magnetic fields. These regions produce a characteristic curve of $\chi(T,H)$ (symmetric in shape approaching a maximum value of $\sim 10^{-5}$ emu/g—enormous for this system) which is observed only at sufficiently low magnetic fields. Time and frequency dependencies of $\chi(T)$ along with x-ray diffraction data provide evidence in favor of a contribution from oxygen ordering to this effect. Crystals with differing excess oxygen content and mobility have been studied and the largest effect has been found in crystals with high oxygen mobility entering the superconducting state.
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The idea that the conduction electron may create a ferromagnetic (FM) region inside an antiferromagnetic (AFM) semiconductor was suggested almost 30 years ago.[1] For high-temperature superconductors (HTSC's) it was shown that for the holes introduced into the CuO plane it is energetically favorable to be surrounded by a ferromagnetically ordered cluster.[2] However, there is as yet no experimental information on the direct observation of the ferromagnetic moment in lightly doped copper oxides at low magnetic fields. The main problem is that one has to measure a specific magnetic susceptibility of 10^{-7} CGSM units of small samples (some cubic millimeters) at temperatures of 200–300 K in a magnetic field of less than 50 Oe. Superconducting quantum interference devices have a low sensitivity threshold but are very susceptible to changes in ambient parameters and the field must be substantially increased in order to work confidently at temperatures of 200–350 K where the transition to the Néel state and phase separation occur in La_2CuO_{4+x}.[3–5] There is an elegant way to increase the sensitivity of a magnetometer with the aid of double synchronous detection.[6,7] During the measurements, the sample, located in a weak ac magnetic field $h=h_0\sin(\omega t)$, moves periodically from one detection coil into another, the coils being connected in opposite directions to one another. As a result, amplitude modulation of the high frequency signal arises. The degree of modulation is proportional to χ_{ac}. In our measurements $h_0=0.1-30$ Oe, $\omega=100$ Hz–10 kHz, and the sample vibrates with a frequency of 2.5 Hz. The temperature was varied over the range 4.2–350 K and a dc magnetic field of 0–450 Oe was applied parallel and perpendicular to the ac field. With this technique we observed a FM transition in lightly doped La_2CuO_{4+x} in low magnetic fields and showed that oxygen ordering is an essential factor to produce the phenomenon.

The La_2CuO_{4+x} single crystals used in the present work were either grown by the floating zone method[8] (FZM) under oxygen pressures of 8 atm at a crystallization rate of about 0.5 mm/h or by the molten solution (MS) method.[9] Crystals grown by FZM can be easily doped with oxygen up to the appearance of superconductivity (with $T_c^{\text{onset}}=40$ K). In contrast, it is very hard to insert extra oxygen in crystals grown by the MS method and to create a noticeable excess oxygen content they were oxygenated in a homemade high-pressure cell. In the present work we studied three crystals with different oxygen content: two dielectrics L1 and L2 grown by the MS method and one superconductor L3 grown by FZM. L1 is the as-grown crystal with $T_N=240$ K and experienced no oxygen treatment. L2 was oxygenated in the high pressure cell ($P_{O(2)}=3$ kbar, $T=600\,^\circ$C) for two days and had some additional treatment at low temperatures after that. The L3 crystal was treated in an oxygen atmosphere ($P_{O(2)}=5$ bar, $T=500\,^\circ$C) for some hours and according to magnetic measurements contained about 10% of the superconducting phase. All three crystals were thoroughly studied by x-ray diffraction, on the base of which the excess oxygen content was estimated to be 0.005 ± 0.003, 0.010 ± 0.003, and 0.013 ± 0.003 for the L1, L2, and L3 crystals, respectively.

Figure 1 shows normal-state $\chi(T)$ data for the superconducting L3 (a) and dielectric L2 (b) crystals with increasing dc magnetic field H from 0 up to 450 Oe. The huge susceptibility, in maximum almost an order of magnitude larger than in the paramagnetic state, is observed for $La_2CuO_{4.013}$ crystal [Fig. 1(a)] when only a weak ac magnetic field is applied. This effect is observed only when the field is parallel to the c axis (*Bmab* space group). In an applied dc magnetic field $H=20$ Oe the peak decreases to a marked degree and in $H=100$ Oe the peak becomes the same as is observed in the AFM state in a strong magnetic field. The lowest curve in Fig. 1(a) was taken when the magnetic field (dc and ac) was applied in the CuO plane and shows no noticeable dependence on the dc magnetic field in the region of 0–450 Oe. The sample L3 is superconducting as is seen from the inset of Fig. 1(a). The dielectric crystal L2 displays the same effect [Fig. 1(b)] in the same magnetic-field interval and addi-

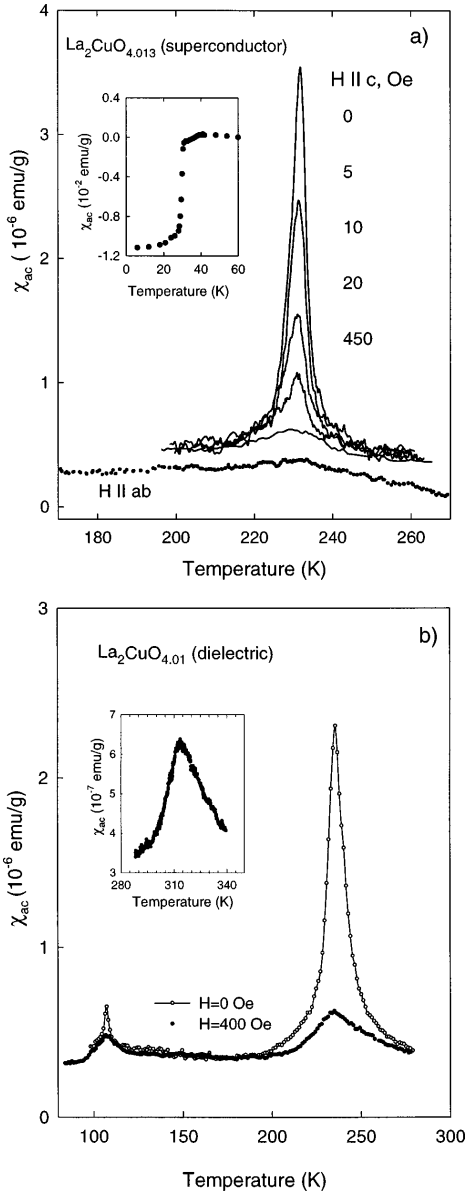

FIG. 1. (a) The magnetic susceptibility $\chi(T)$ of the superconducting L3 crystal measured in dc magnetic fields ($0<H<450$ Oe) for the $H\|c$ and $H\|ab$ orientations (for the $H\|ab$ orientation the susceptibility does not change with the dc magnetic field, so only one curve is shown). The inset shows the diamagnetic response of the same crystal. (b) The magnetic susceptibility $\chi(T)$ of the dielectric L2 crystal presented for the lowest and highest magnetic fields $H=0$ (solid line) and $H=400$ Oe (experimental points). The inset shows the magnetic susceptibility of L2 after high-temperature annealing in an inert atmosphere ($T=700$ °C, $t=10$ h). The amplitude of the ac magnetic field was $h_0=3$ Oe.

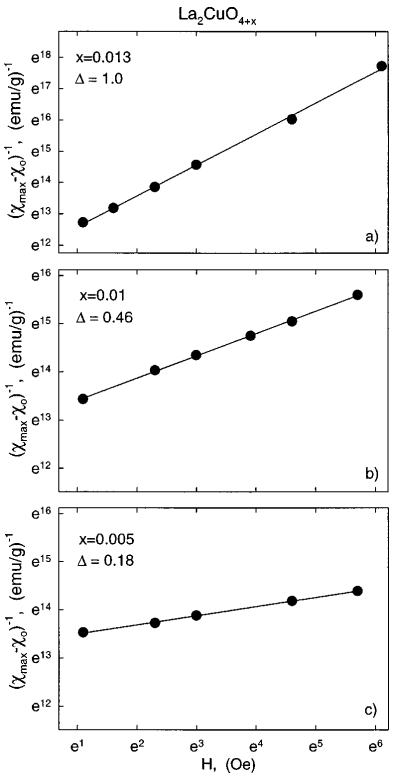

FIG. 2. The inverse magnetic susceptibility for L3 (a), L2 (b), and L1 (c) corrected to the background value (the peak at the AFM transition in high magnetic fields) as a function of the dc magnetic field H. One can see the universal behavior $\chi_{\max}^{-1}\sim H^{\Delta}$ with the Δ value presented for each sample.

tionally to the main peak at 240 K, demonstrates one more peak at low temperatures near $T=110$ K signaling the presence of a magnetic transition. This small peak is also sensitive to the applied magnetic field, implying that both peaks have a similar origin (see below). One can observe that at low magnetic fields the main peak has a symmetric shape resembling a ferromagnetic transition while with increasing magnetic field this peak approaches its asymmetric shape. It is worth mentioning that annealed in an inert atmosphere, and thus stoichiometric, crystals [inset of Fig. 1(b)] have the same intensity and the shape of the AFM peak as the oxygen-doped are measured in a magnetic field of 400–450 Oe [Figs. 1(a) and 1(b)]. The asymmetric shape is characteristic of the Néel state with canting magnetic moments in La_2CuO_{4+x}. This canting, together with the exponential temperature dependence of the two-dimensional correlation length, accounts quantitatively for the asymmetric susceptibility peak at the Néel temperature.[10,11] The as-grown dielectric crystal L1 displays the same effect of anomalous enhancement of susceptibility in low magnetic fields but the effect is smaller than for the oxygenated crystals L2 and L3. The magnetic-field dependence of the maximum of $\chi(T)$ for all three crystals is shown in Fig. 2 where χ_0 corresponds to the peak at the AFM transition in high magnetic fields corrected to the background value. All crystals demonstrate the universal behavior $\chi_{\max}^{-1}\sim H^{\Delta}$ with Δ depending on the oxygen content. The next important finding is the time dependence of the main peak which is possible to observe even at room temperature [Fig. 3(a)], because the time scale is large enough in this case. In Fig. 3 data are presented for the L2 crystal where the oxygen mobility is sufficiently low that the oxygen diffusion and oxygen ordering take a long enough time to be observed. The process can be speeded up by heating the crystal to 100–200 °C (where there is not yet any oxygen depletion and only redistribution occurs). These various temperature data sets allow us to evaluate the oxygen activation energy and relaxation time by using the equations $\chi_{\max}=\chi_0\exp(t/\tau)$ and $\tau=\tau_0\exp(E_a/T)$. The activation energy $E_a=0.28$ eV is in good agreement with the rough estimate (0.25 eV) obtained in a ^{139}La NQR study[12] and with the value (0.24 eV) obtained from a static magnetic susceptibility study.[5]

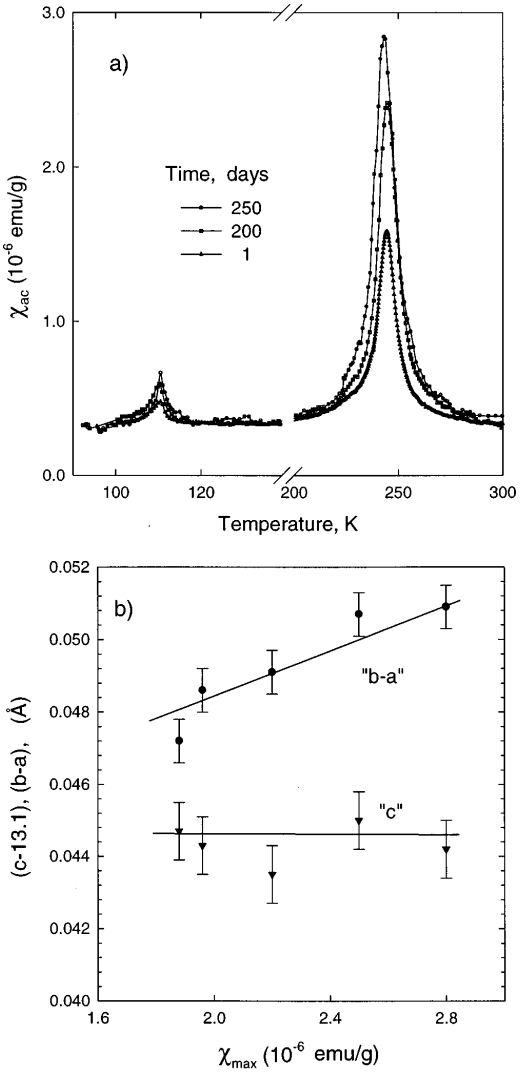

FIG. 3. (a) The time evolution of the magnetic susceptibility $\chi(T)$ of (L2). Between the measurements the crystal was kept at room temperature. (b) The orthorhombicity $(b-a)$ and c-axis parameter for L2 as a function of susceptibility peak intensity. The lines are drawn as a guide for the eye.

In addition, the lattice parameters were also measured, simultaneously with the susceptibility. Figure 3(b) shows the lattice parameters as a function of susceptibility peak intensity, with the time as a hidden parameter. While orthorhombicity $(b-a)$ goes up with time, the c-axis value remains the same within the measured experimental error. The latter shows that the excess oxygen content is conserved in the sample, whereas the $(b-a)$ dependence is a sign of oxygen ordering at room temperature.

With our modulation technique it is possible to carry out ac susceptibility measurements at different frequencies. The ferromagnetic peak grows with decreasing frequency and approaches extremely high values of 6.5×10^{-6} emu/g for the L3 crystal. Figure 4 shows the frequency dependence of the normalized (to the maximum at 100 Hz) susceptibility on all three crystals measured.

The crystals used in the present work have different excess oxygen mobility. The highest is in the crystal grown by the FZM (L3) where a superconducting response was observed in as-grown samples and the excess oxygen content

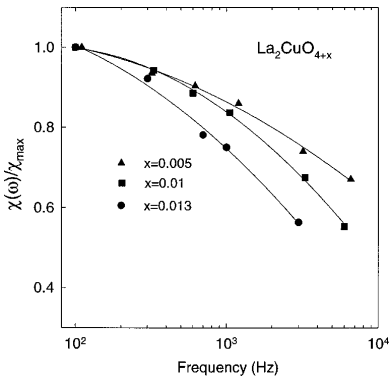

FIG. 4. The magnetic susceptibility of L1 (triangles), L2 (squares), and L3 (circles), normalized to the peak intensity at lowest measured frequency of 100 Hz, plotted versus the frequency of the ac magnetic field. $h\|c$ with $h_0=3$ Oe. The lines are drawn as a guide for the eye.

can be changed easily and reversibly at rather low oxygen pressures. The whole ''T-x'' phase diagram of crystals grown by the MS method is quite different because of their low oxygen mobility. L1 and L2 belong to this series of samples. It is known that sample quality is crucial for the oxygen diffusion process. In Ref. 13 it was shown that oxygen insertion in La_2CuO_{4+x} thin films first happens mainly along planar faults and dislocations and only after this does a very slow oxygen diffusion along the interstitial sites take place. So we do expect diminished oxygen mobility in high-quality single crystals because of the lack of structural channels for diffusion process. As a result, it was possible to get macroscopically nonseparated superconducting crystals whose excess oxygen concentration is inside the miscibility gap.[14,15] That is why the appearance of superconductivity is not only a question of excess oxygen content (crystals L2 and L3 have close concentration of oxygen) but of oxygen mobility as well. This mobility to some extent is important for other properties, e.g., the time dependence of the susceptibility (Fig. 3) clearly shows that oxygen ordering (which is dependent of the oxygen diffusion) affects the peak intensity. That is why the maximum effect is observed in the crystal with highest oxygen mobility (L3) where extra oxygen atoms can freely diffuse. The frequency dependence of the peak intensity (Fig. 4) also can be explained in this framework, being largest in L3 and at least two times slower in L1. It was shown in Ref. 16 for systems having a relaxation-time distribution $\tau_0,\ldots,\tau_{\max}$ that the dependence of the physical quantities on the time, in contrast to the usual relaxation law $M(t)=M(0)\exp(-t/\tau)$, is given by $M(t)=M(0)\exp[-(t/\tau)^{\gamma}]$, where $0<\gamma<1$. Such a relaxation law was observed in spin glasses. This spin-glass-like behavior is expected for the crystals with low oxygen mobility to which L1 belongs. As concerns the microscopic mechanism responsible for the process of susceptibility enhancement, it is worth considering one connected with the oxygen ordering, taking into account the time dependence of the lattice parameters [Fig. 3(b)].

Upon being introduced into the CuO_2 plane, holes form a ferromagnetic cluster[2,17] due to a local ferromagnetic exchange coupling between Cu spins. A specific property of oxygen-doped La_2CuO_{4+x} is that there are two inequivalent positions $(\frac{1}{4},\frac{1}{4},z)$ and $(\frac{3}{4},\frac{3}{4},z)$ in the *Bmab* space group for extra oxygen in the lattice.[18] In each position the oxygen

hole creates a ferromagnetic ordering of the copper spins in its immediate environment but these magnetic moments are opposite to each other for the two positions. So if the extra oxygen atoms occupy these positions with equal probability, all ferromagnetic moments over the crystal are cancelled. In turn, if these occupancies are different, a noncompensated moment is expected to appear. The situation is close to that in ferrimagnetic substances. In this case the magnetic-field dependence can be treated as a phase transition in the magnetic field with different critical indices for different samples. These critical indices highlight the differences between the different crystals. The maximal critical exponent $\Delta = 1$ [Fig. 2(a)] is in the crystal with the highest oxygen mobility (L3), implying that the magnetic moment $M = \chi H$ is already saturated in low magnetic fields, i.e., oxygen ordering plays in some sense the role of a magnetic field in aligning the ferromagnetic moments. The lower the oxygen diffusion and excess oxygen content, the more the oxygen impurity atoms in the lattice are scattered and the larger the magnetic field that is needed to align the magnetic moments. In the framework of this treatment it is possible to explain the presence of the second magnetic peak at 110 K as a result of magnetic compensation in a ferrimagnetic lattice. Earlier this peak was assigned to a freezing of small fluctuations of the Cu spins.[19] The present explanation of this low-temperature magnetic transition seems more natural.

One can evaluate the magnetic moment for the ferromagnetic state from the magnetic-field dependence of the susceptibility (Fig. 2) and orthorombicity [Fig. 3(b)]. $M(H)$ can be deduced from the magnetic-field dependence of the susceptibility simply by integrating $\chi(H)$. The saturation moment for L2 calculated for each Cu atom is $3\times10^{-6}\ \mu_b$ by this procedure, which is about 0.1% of the canting moment for the Cu spins in the AF lattice. The moment can also be evaluated from the change of the orthorombicity with oxygen ordering [Fig. 3(b)] if one takes into account that the orthorhombicity parameter is directly connected with the tilting angle ϑ of the CuO_6 octahedra: $(b-a)\sim\vartheta^2$ (Ref. 20) and in turn, this tilting angle is proportional to the canting magnetic moment of the Cu spin. The calculation gives a magnetic moment of $5\times10^{-6}\ \mu_b$ which is very close to the moment deduced from the $M(H)$ dependence. The main question left unanswered in this picture is how and to what extent magnetism and superconductivity coexist in La_2CuO_{4+x} since the magnetic moment and conductivity at low doping seem to have the same cause—holes introduced into the AFM matrix. The experimental fact is that the effect of anomalous susceptibility is only observed in lightly doped La_2CuO_{4+x} ($x<0.015$), while for the phase separated samples with the larger oxygen content $x=0.04$ well inside the miscibility gap ($0.01<x<0.06$) the ordinary weak asymmetric AFM peak is observed in a weak ac magnetic field.[21] The most intriguing question here is when and how the crossover from the weak FM to ordinary AFM state happens in phase-separated crystals in the weak magnetic fields.

In conclusion, we have observed a weak ferromagnetic transition in lightly doped La_2CuO_{4+x} single crystals in low magnetic fields using ac magnetic susceptibility. The transition has been observed in both phase-separated (superconducting) and non-phase-separated (dielectric) crystals and the effect is suggested to be due to oxygen ordering in La_2CuO_{4+x}.

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*Permanent address: Russian Scientific Center ''Kurchatov Institute,'' 123182, Moscow, Russia.

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