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Magnetic properties of the superconducting "superoxide" $La_2CuO_{4+\delta}$

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The magnetic properties of $La_2CuO_{4+\delta}$ ($\delta \leq 0.13$) have been determined by means of muon-spin rotation and relaxation in transverse and zero external fields. A fraction $f_{SC} = 0.6$ of the sample was found to be superconducting with $T_c = 35(1)$ K and extrapolated penetration depth $\lambda(0) = 4200$ Å (powder average). The other phase, 40% of the sample volume, displayed static magnetic ordering identical to that of oxygenated La_2CuO_4. The T dependence of λ is similar to that for samples of the $La_{2-x}Sr_xCuO_4$ family.

Utilizing the muon as a local interstitial point probe of internal field distributions, the muon-spin-relaxation (μSR) technique has recently yielded unique determinations of magnetic penetration depths λ in the oxide superconductors (for example, in the $La_{2-x}Sr_xCuO_4$ series[1,2]) and of the ordering parameters for the related antiferromagnetic precursors.[3-7] In this paper we present the first μSR results on the "superoxide" $La_2CuO_{4+\delta}$.

The sample was prepared at Sandia National Laboratories as described in detail in previous publications.[8,9] Briefly, the superconducting material is obtained by high-pressure annealing of a La_2CuO_4 sample (3 kbar at 500 °C) for 62 h in oxygen. The as-prepared La_2CuO_4 material exhibited filamentary superconductivity since it had been subjected to atmospheric pressure annealing in oxygen gas for 12 h at 900 °C. For the high-pressure annealed samples, susceptibility measurements show that at least 30% of the material is a bulk superconductor, and the structure and electronic state of the extra oxygen have been characterized in a series of experiments as intercalated O_2^-.[8,9] The oxygen excess is nominally $\delta = 0.13$, but, due to surface effects, this should be taken as an upper limit for the bulk of the material. More recently, Jorgensen *et al.* have shown, by means of neutron-diffraction work, that such samples consist of two nearly identical orthorhombic phases.[10] The aim of the present investigation was to determine, by means of μSR, the microscopic magnetic characteristics of the different phases, based on accumulated experience with various samples of the La_2CuO_{4-y} and $La_{2-x}Sr_xCuO_4$ systems. Thus we have performed a series of measurements at zero magnetic field (ZF) and weak (*vis-à-vis* the internal field $\mathbf{H}_\mu^{\text{int}}$) transverse field (WTF) to explore the magnetic ordering, and at high transverse field (HTF) to study the vortex state in the superconducting phase.

The measurements were carried out using "surface" beams at the TRIUMF facility (momentum about 29 MeV/c), and apparatus and techniques similar to those of previous work (for details, see Refs. 1, 7, 11, and 12). An external magnetic field, $\mathbf{H}_{\text{ext}}$ of 100 Oe and 2.5 kOe, was applied perpendicular to the initial polarization of the muons for the WTF and HTF cases, respectively. The experimental quantity determined is the time evolution of the μ-ensemble spin polarization (i.e., asymmetry time histograms) over typically 10 μs after implantation. The asymmetry function in the transverse field consists of a precession signal (Larmor frequency for the muons) modulated by the spin-relaxation function $G_{TF}(t)$. In turn, $G_{TF}(t)$ is the Fourier transform of the line shape due to the microscopic field distribution acting on the muon-spin magnetic moment.[4,13,14]

As described in detail in the previous work, the fraction of the sample which is not magnetically ordered (paramagnetic phase) can best be determined in the WTF arrangement. Therefore, a series of runs was first carried out in a 100-Oe field in the range 5–300 K. Figure 1(a) shows an example of the effect of internal fields on the precession signal. The random but larger internal fields in the ordered (henceforth called AFM) phase give rise to a rapidly decaying modulation of G_{TF}, and the signal remaining at longer times (typically after 1 μs) is due only to the coherent precession of the spin of the muons in the paramagnetic environment. In turn, the polarization of this fraction is damped by the magnetic field distribution in the vortex state and by interaction with nuclear dipoles, but at a slower rate. This served to extract the relative fractions of muons in the paramagnetic and ordered environments. The paramagnetic signal includes contributions from the superconducting (SC) phase as well as from muons stopped in the sample holder. The inhomogeneous broadening, due to the onset of superconductivity, was clearly seen for the fraction f_{SC} of muons in the SC

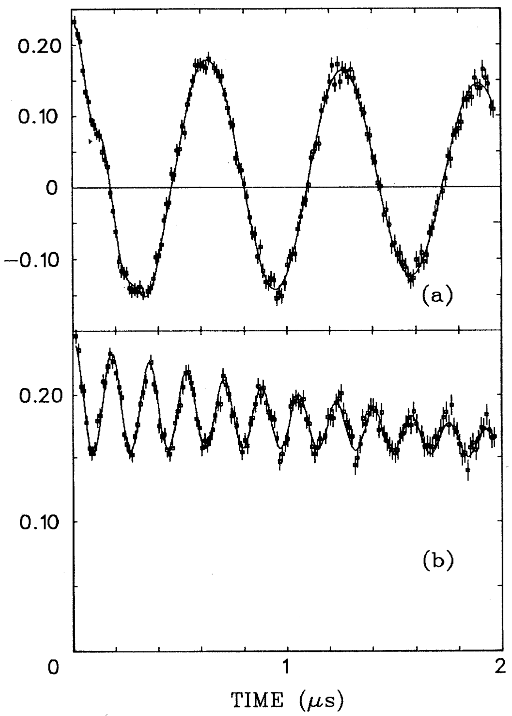

FIG. 1. Examples of 3-signal fits to (a) WTF at 100 Oe and (b) ZF data. Only the first 2 μs of data are shown for clarity of the diagram. Similar results were obtained for the HTF data.

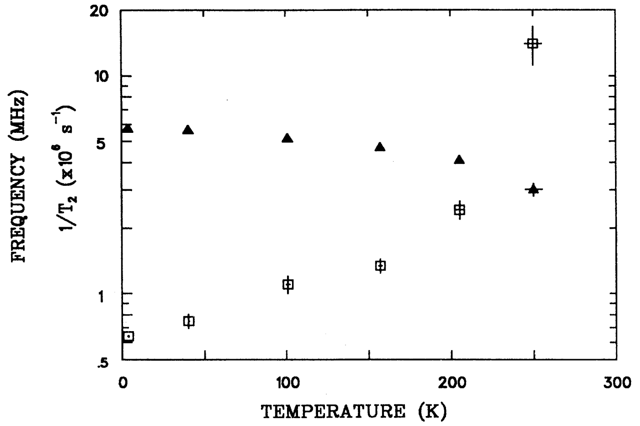

FIG. 2. Results for the precession frequency (MHz, filled triangles) and relaxation rate ($1/T_2$ in μs^{-1}, open squares) of the ZF AFM signal. Notice the vertical scale is the same for both quantities.

phase below 35 K, as was the existence of internal fields for the ordered phase in WTF measurements in the range 5–250 K. The ordered phase was then studied in more detail in a series of ZF runs. In zero applied field the muon polarization precesses in the internal field $\mathbf{H}_\mu^{\text{int}}$ due to the ordered ionic moments in the AFM state. The observation of a discrete frequency with little depolarization, an example of which is shown in Fig. 1(b), indicates that the internal field at the muon site is unique and quasistatic within the μSR time window, its random orientation reducing the amplitude of the oscillation. The depolarization observed is due to inhomogeneous broadening as the internal AFM field has a finite distribution width. The rest of the muons (stopping both in the SC phase and the sample holder) contribute a slowly varying background, depolarized only by nuclear dipolar interactions. Since the measurements were taken from high temperatures, there is no effect due to the onset of superconductivity. From the ZF data, the temperature dependence of the internal field and depolarization rate for the muons in the AFM phase were extracted from 3-signal fits and are shown in Fig. 2 as frequency and relaxation rate $1/T_2$, respectively. The low-temperature value of the frequency corresponds to $H_\mu^{\text{int}} = 430$ Oe, and the signal disappearance at 295 K indicates a spin-freezing temperature in the range $250 < T_f < 295$ K. The data of Fig. 2 are practically indistinguishable from that for phase-pure La_2CuO_4 samples.[3–7]

The penetration depth λ of the SC phase was determined from the relaxation of the muon spin polarization signal in an external field $\mathbf{H}_{\text{ext}}$, such that the separation between the vortices in the resulting vortex state is smaller than λ. Given the small value of the coherence length ξ, the vortices are still well separated, and the associated large H_{c2} implies that the simple London picture $[H_{c1} \ll H_{\text{ext}} \leq (H_{c2}/4)]$ is valid for the 2.5-kOe field used in the present work. Under such conditions, the μ-spin re-

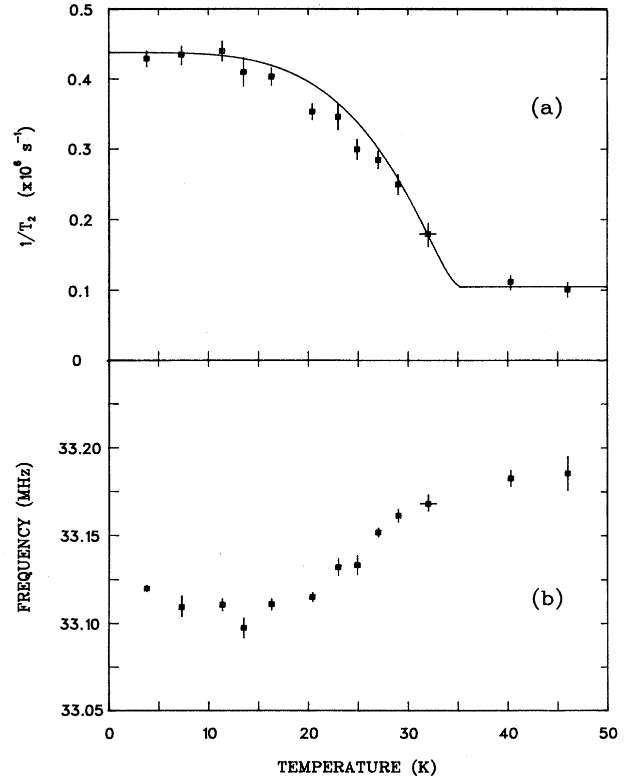

FIG. 3. Depolarization rate ($1/T_2^{SC}$ in μs^{-1}) and mean frequency for the SC fraction. The solid line was calculated from Eqs. (1) and (2) as described in the text, i.e., it corresponds to conventional nodeless gap superconductivity.

laxation rate is independent of $\mathbf{H}_{\text{ext}}$ and given by the second moment $M_2 = \langle |\Delta H|^2 \rangle^{1/2}$, of the microscopic field distribution, analogous to the field inhomogeneity broadening in magnetic resonance. For a Gaussian field distribution, the muon-polarization line shape is also Gaussian, $G_{\text{TF}}(t) = \exp(-t^2/T_2^2)$, which was shown to be a good approximation for polycrystalline samples.[14] From the relaxation time T_2^{SC} the magnetic penetration depth is determined by the relation[15]

$$\lambda = \sqrt{0.043 \phi_0 \gamma_\mu T_2^{\text{SC}}} , \qquad (1)$$

where ϕ_0 is the magnetic-flux quantum and $\gamma_\mu = 2\pi \times (13.55 \text{ MHz/kOe})$ is the muon's gyromagnetic ratio.

The HTF data were also analyzed using three components for the asymmetry signal. The component due to the AFM fraction is rapidly depolarized, and its effect is negligible after 500 ns, while the background signal shows only a very small depolarization, consistent with its originating in the Al sample holder. The relative amplitudes of the three signals were the same, within errors, for the three cases (WTF, ZF, and HTF) analyzed independently. This yielded a ratio of 3:2 for the SC to AFM volume fraction ratio, which implies a $f_{\text{SC}} = 0.6$ volume fraction for the SC phase assuming only two phases in the sample, which is in excellent agreement with the neutron-diffraction work.[10] Figure 3 shows the obtained relaxation rate and fitted average frequency for the SC signal. The onset of the diamagnetic frequency shift is itself an independent indication of the formation of the vortex state. The relaxation rate is compared for reference to the temperature dependence given by the empirical relation

$$\lambda(T) = \lambda(0)[1 - (T/T_c)^4]^{-1/2} , \qquad (2)$$

in conjunction with Eq. (1), and with the dipolar depolarization added in quadrature. Thus, for the SC phase we obtain $T_c = 35(1)$ K, in rough agreement with the magnetization and resistivity critical temperatures,[9,10] and a powder average penetration depth of $\lambda(0) = 4200$ Å. It should be noted that Eq. (1) yields penetration depth values about 17% larger than the expression used in the earlier work[1,2] [see Brandt (Ref. 15) for details]. In the London picture, $\lambda(0) \propto (n_s/m^*)^{0.5}$, from which we extract a value of 10^{21} cm^{-3} for the superconducting carrier density n_s, assuming an effective mass $m^*/m_e = 7$ from the $La_{1.85}Sr_{0.15}CuO_4$ case,[1] in agreement with the hole number density produced by the extra oxygen.

In conclusion, we have determined the magnetic properties of a two-phase $La_2CuO_{4+\delta}$ sample of nominal composition $La_2CuO_{4.13}$. The relative fraction and critical temperature of the SC phase were in agreement with the neutron-powder-diffraction study on samples from the same source. In addition, we have determined a powder average value of 4200 Å for the London penetration depth. The T dependence of λ is slightly different from that given by Eq. (2) as was also found to be the case for $La_{1.85}Sr_{0.15}CuO_4$ and oxygen deficient $YBa_2Cu_3O_{7-x}$, i.e., inhomogeneous samples. Such departure has been interpreted theoretically in terms of the strong coupling approximation[16,17] for singlet pairing superconductivity. The other phase was found to display identical internal fields and T dependence of those of stoichiometrically pure $La_2CuO_{4.0}$, thus confirming the assignment of Jorgensen *et al.*,[10] in which the major phase was assumed to be superconducting. No direct evidence was found for the interaction of muons with the intercalated O_2^- species.

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