Tuning the Interlayer Spacing of High-T_c Bi-Based Superconductors by Intercalation: Measuring the Penetration Depth and the Two-Dimensional Superfluid Density

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Substantial control of the interlayer spacing in Bi-based high temperature superconductors has been achieved through the intercalation of guest molecules between the superconducting layers. Measurements using implanted muons reveal that the penetration depth increases with increasing layer separation while T_c does not vary appreciably, demonstrating that the bulk superfluid density is not the determining factor controlling T_c. Our results strongly suggest that for Bi-based high temperature superconductors the superfluid density appearing in the Uemura scaling relation $\rho_s \propto T_c$ should be interpreted as the two-dimensional density within the superconducting layers, which we find to be constant for each class of system investigated.

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A fundamental property of high temperature superconductors (HTSs) is the presence of CuO_2 planes with some degree of weak coupling between them [1]. The nature of this coupling [2] has been debated in the past and an understanding of the effective dimensionality of the HTSs remains a priority. The Uemura relation between the superconducting transition temperature and the bulk superfluid density ($T_c \propto \rho_s \propto n_s/m^*$) has been found to apply to a range of underdoped cuprates [3]. However, in the majority of systems, the average spacing between CuO_2 planes lies within the narrow range 0.6 ± 0.1 nm, so it is difficult to separate two-dimensional (2D) and three-dimensional (3D) phenomena [3–5]. No clear trends in the 2D superfluid density emerged when a variety of materials with unusual layer spacing have been compared in the past [5,6], though it is likely that, in these cases, factors beyond the superfluid density influence T_c. To address the question of dimensionality experimentally we have modulated the interlayer coupling of the CuO_2 planes in two HTS materials by intercalating molecular groups between the layers, which does not perturb the superconducting blocks. Here we present the results of a muon spin rotation (μ^+SR) investigation of the evolution of the penetration depth (and hence ρ_s) with layer separation in these systems. We are able to demonstrate that the bulk superfluid density ρ_s is not the parameter controlling T_c and that the superfluid density appearing in the Uemura relation should be interpreted as the superfluid density within the 2D superconducting layers, which is independent of the layer separation.

The bismuth based cuprates possess weakly bound Bi_2O_2 double layers that allow the intercalation of guest molecules without any substantial change in the superconducting block [7–12]. Weak interaction between the guest molecule and host layers ensures that the intercalation process does not distort the superconducting layers. This overcomes a substantial difficulty with alternative attempts to control the interlayer spacing [13], which involve the sequential deposition of superconducting and insulating layers. Moreover, the intercalation of long chain organic molecules [shown schematically in Fig. 1(a)] [8,9] allows the possibility of tuning the layer (or bilayer) separation d on a scale fixed by the length of the hydrocarbon chain. Organic guest species electrically isolate the layers since organic molecules are, in general, very good insula-

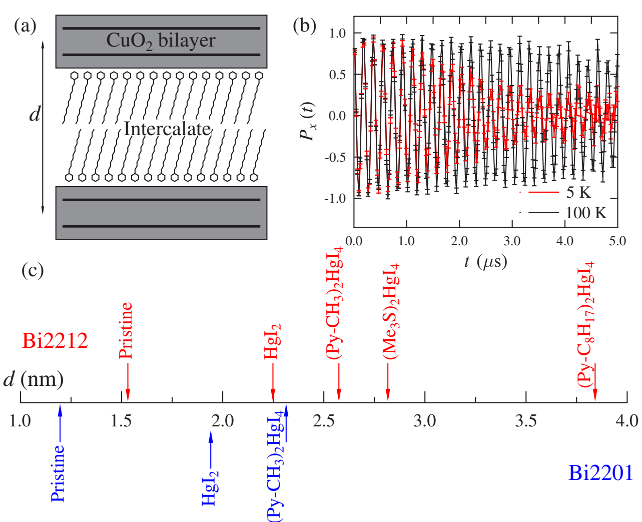

FIG. 1 (color online). (a) Schematic of the Bi2212 intercalates with molecular groups acting to separate the CuO_2 bilayers. (b) TF μ^+SR spectra measured in 40 mT above and below T_c for intercalated Bi2212 with $d = 2.61$ nm. The stronger relaxation for $T < T_c$ is caused by the distribution of fields in the vortex lattice. (c) Interlayer-bilayer separation d for each intercalate studied.

tors. In this Letter we examine intercalation series based on two classes of Bi-based superconductors, namely, bilayer $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ (Bi2212) and single layer $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\epsilon}$ (Bi2201). Previous work on these classes [7–12] has suggested that while the intercalation of guest species allows d to be varied by a factor of 3, the transition temperature of the intercalated materials does not vary appreciably compared to the pristine compound.

Transverse field muon spin rotation (TF μ^+SR) provides a means of accurately measuring the internal magnetic field distribution caused by the vortex lattice (VL) in a type II superconductor [14]. The vortex state of the pristine polycrystalline Bi2212 and Bi2201 systems has been studied with μ^+SR previously [5,15,16]. In a TF μ^+SR experiment, spin polarized muons are implanted in the bulk of a superconductor, in the presence of a magnetic field $B_{c1} < B < B_{c2}$, which is applied perpendicular to the initial muon spin direction. Muons stop at random positions on the length scale of the VL where they precess about the total local magnetic field B at the muon site (mainly due to the VL), with frequency $\omega_\mu = \gamma_\mu B$, where $\gamma_\mu = 2\pi \times 135.5$ MHz T^{-1}). The observed property of the experiment is the time evolution of the muon spin polarization $P_x(t)$, which allows the determination of the distribution $p(B)$ of local magnetic fields across the sample volume via $P_x(t) = \int_0^\infty p(B)\cos(\gamma_\mu Bt + \phi)dB$, where the phase ϕ results from the detector geometry.

Powder samples of several intercalates of Bi2212 and Bi2201 were prepared as reported previously [7–10]. The intercalates studied and the separation d of CuO_2 layers (or bilayers) achieved are given in Fig. 1(c) and Table I. μ^+SR measurements were made at the ISIS facility using the MuSR spectrometer and the SμS facility using the GPS spectrometer. Samples were pressed into pellets and mounted on hematite to reduce the background.

Figure 1(b) shows TF μ^+SR spectra measured above and below T_c for intercalated Bi2212 ($d = 2.61$ nm) in an applied field of 40 mT. Above T_c some slight broadening of the spectrum is caused by randomly directed nuclear moments relaxing the muon spins. Below T_c the spectrum broadens considerably due to the contribution from the VL. The expected width of the field distribution in the powder sample was estimated using the numerical results reported for the field width in the Ginzburg-Landau (GL) model that were obtained for a field normal to the layers [17]. A polycrystalline average was taken under the assumption that the length scales λ and ξ diverge following $1/\cos\theta$ as the field orientation approaches the plane at $\theta = 0$ (high anisotropy limit), with the corresponding contribution to the overall width scaling as $\cos\theta$. Fitting our data with these results allowed us to extract the second moment of the distribution, B_{rms}, at each measured field and temperature, and relate it to the vortex properties and penetration depth of the material.

Figure 2(a) shows the temperature dependence of B_{rms} in an applied field of 5 mT for each intercalate studied. For both series, the magnitude of B_{rms} falls continuously with increasing temperature to a low constant value for $T \geq T_c$. The exceptions are the materials with the largest layer separation d in each series (discussed below). Fits are shown to an empirical power law functional form [16]

$$B_{rms}^2(T) = B_{VL}^2(0)[1 - (T/T_c)^r]^2 + B_{bg}^2, \quad (1)$$

where $B_{VL}(0)$ is the zero temperature contribution from the VL and B_{bg} represents a background contribution from the dipole fields from nearby nuclei. The parameters derived from these fits are given in Table I. There is little variation in T_c while $B_{VL}(0)$ decreases smoothly with increasing layer spacing. The curvature parameter r falls within the range $2 \leq r \leq 6$, which is a slightly larger range than that previously observed when this approach was applied to $YBa_2Cu_3O_x$ (YBCO) [16]. The background contribution B_{bg} is within the range found for pristine materials [15,16], confirming that the intercalant is not introducing significant broadening.

The magnetic field dependence of B_{rms} [18] measured at low temperature for each series is shown in Fig. 2(b). The general trend is for B_{rms} to increase sharply with increasing

TABLE I. Properties of the intercalates of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ (Bi2212) and $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\epsilon}$ (Bi2201), with parameters derived from the fitting routines described in the main text (Py, pyradine; Me, methyl). Fits were not possible for the materials with largest d from each class, although their T_c values (derived from magnetization measurements) coincide with those of the respective series to within ~1 K [8].

Class	Intercalant	d (nm)	T_c (K)	r	$B_{VL}(0)$ (mT)	B_{bg} (mT)	λ_{ab} (nm)	ξ (nm)	d/λ_{ab}^2 (10^4 m^{-1})
Bi2212	None	1.53	82.4(2)	4.6(6)	1.52(5)	0.07(2)	200(6)	6(1)	3.8(2)
	$[HgI_2]_{0.5}$	2.25	80.6(1)	5.7(4)	1.30(3)	0.09(1)	230(10)	···	4.3(4)
	$[(Py\text{-}CH_3)_2HgI_4]_{0.35}$	2.61	79.0(1)	2.6(1)	1.04(1)	0.11(1)	271(7)	3(1)	3.6(2)
	$[(Me_3S)_2HgI_4]_{0.34}$	2.79	88(3)	2.1(3)	0.90(6)	0.07(1)	270(8)	···	3.8(2)
	$[(Py\text{-}C_8H_{17})_2HgI_4]_{0.35}$	3.82	···	···	···	···	···	···	···
Bi2201	None	1.21	22.1(2)	3.0(2)	0.98(3)	0.006(3)	290(8)	13(3)	1.44(8)
	$(HgI_2)_{0.5}$	1.92	22.3(5)	2.1(3)	0.63(5)	0.05(3)	370(10)	10(2)	1.40(8)
	$[(Py\text{-}CH_3)_2HgI_4]_{0.35}$	2.30	···	···	···	···	···	···	···

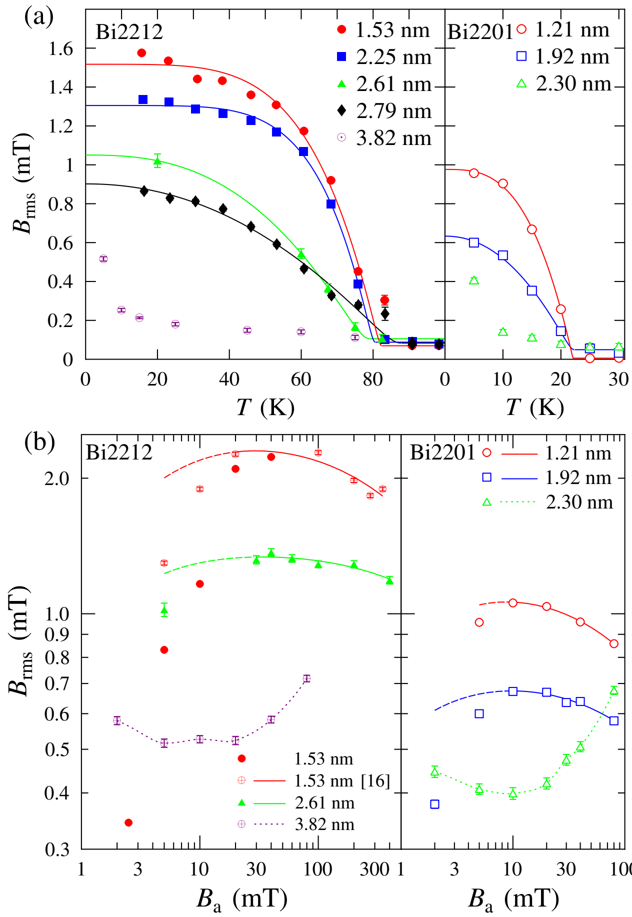

FIG. 2 (color online). (a) Temperature dependence of $B_{\rm rms}$ for Bi2212 (left) and Bi2201 (right) intercalates with $B_a = 5$ mT. Fits are described in the main text. (b) The evolution of $B_{\rm rms}$ with applied field at $T = 5$ K (Bi2201) and $T = 20$ K (Bi2212) with additional data for pristine Bi2212 obtained from Ref. [16]. Fits are shown with a solid line for the range over which the fitting was carried out; extrapolations are shown with a dashed line. The materials with the largest layer separations show markedly different behavior in both temperature and applied field (dotted lines are guides to the eye).

field before describing a broad peak and decreasing for high fields. Again the exceptions to the general behavior occur for the largest layer separation d.

Our measurements allow us to extract the in-plane penetration depth λ_{ab} $(=\sqrt{\lambda_a \lambda_b})$ which results from those supercurrents flowing within the superconducting layers [14]. This is achieved by comparing the field dependence of $B_{\rm rms}$ with the behavior expected for the GL model [Fig. 2(b)] [17]. The model describes the data well for fields around the peak value of $B_{\rm rms}$ and above, but provides a poor description of the data at low fields (probably due to the anisotropic magnetization and the distribution of demagnetizing factors in the differently aligned crystallites). We note that the ξ dependence of the theoretical line width becomes very weak near the peak, making an accurate assignment of ξ unimportant in our discussion of λ_{ab}.

Indeed, close to the expected peak in $B_{\rm rms}$, for the high κ regime (as is the case for our systems), the GL model predicts the well-known result $B_{\rm rms}^2 = 0.00371\Phi_0^2\lambda^{-4}$ [14,17]. (Here, the penetration depth λ should be interpreted as the effective penetration depth which includes contributions from supercurrents both parallel and perpendicular to the layers.) The values of λ_{ab} and ξ derived from our data are given in Table I [19]. As above, we were not able to model the samples with the largest d for each class of material.

The general trend revealed by our measurements is a clear increase in λ_{ab} with increasing layer separation d. In the clean limit, we expect $\lambda^{-2} \equiv \rho_s = \mu_0 e^2 n_s/m^*$, where ρ_s is the bulk superfluid density; thus, ρ_s decreases with increasing d, but crucially T_c remains almost unchanged. This strongly suggests that for Bi-based HTSs the bulk superfluid density is not the determining factor controlling T_c. We note that our results differ from those which involve varying the thickness of a $PrBa_2Cu_3O_7$ (PBCO) layer in PBCO-YBCO superlattices, where it was found that $T_c \propto 1/d$ [6,13]. We stress, however, that chemical intercalation should produce undistorted superconducting layers (see above).

The behavior we observe contrasts with that expected from a simple application of the Uemura scaling relation $T_c \propto \rho_s \propto n_s/m^*$ [3] which holds for many underdoped superconductors [Fig. 3(a)]. This scaling relation is, however, often interpreted as suggesting the strong two dimensionality of the superfluid in underdoped cuprate

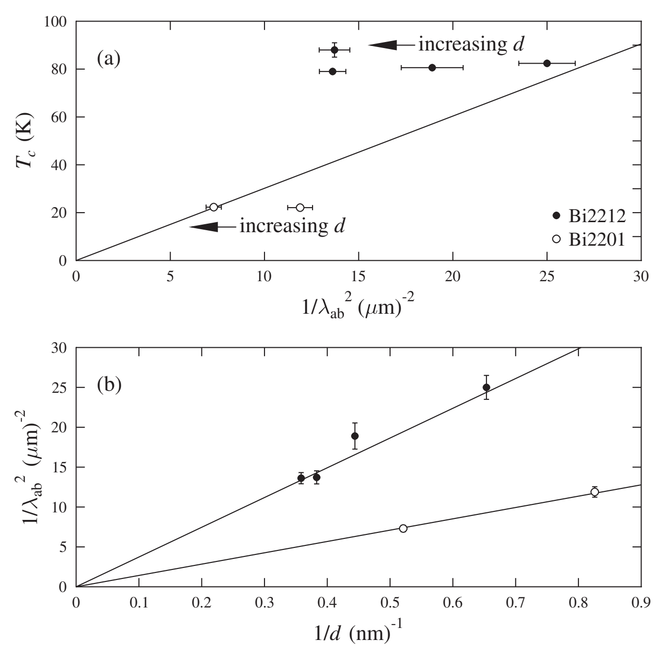

FIG. 3. (a) Uemura plot of T_c vs $1/\lambda_{ab}^2$ for our compounds. The solid line represents the scaling proposed for the underdoped cuprates [3]. (b) The variation of the penetration depth λ_{ab} with the inverse layer separation $1/d$ gives a straight line dependence for each series, suggesting the constancy of $d/\lambda_{ab}^2 (\propto \rho_{s2D})$.

superconductors [4]. We might, therefore, expect that for the intercalated systems $T_c \propto \rho_{s2D}$, where ρ_{s2D} is the superfluid density in the superconducting layers. If we assume that the superfluid density in each CuO_2 layer is the same for each class of material (i.e., a constant for Bi2212 and a different constant for Bi2201), then we should expect that $d/\lambda_{ab}^2 \propto \rho_{s2D} \propto T_c$. We see from Table I and Fig. 3(b) that our data are quite well described by this assumption: d/λ_{ab}^2 is approximately constant for each class of materials, as is T_c. This strongly suggests that the superfluid density appearing in the Uemura relation should be interpreted as the 2D density in the superconducting planes in these Bi-based HTSs.

Some insight into the meaning of our results may be obtained if we assume that underdoping destroys superconductivity at a quantum critical point (QCP) in these systems. Near a QCP [20,21] an energy scale such as T_c should vary as $T_c \propto \delta^{z\nu}$, where δ is the difference in doping from the QCP, z is the dynamic exponent, and ν is the correlation length exponent. Combining this with the prediction of Josephson scaling near a QCP, $\rho_s(0) \propto \delta^{(z+D-2)\nu}$, we have $T_c \propto \rho_s(0)^{z/(z+D-2)}$. For $D = 2$ this predicts Uemura scaling $T_c \propto \rho_{s2D}$ [20]. Our findings may therefore be suggestive of the influence of 2D quantum fluctuations in the underdoped regime.

Finally we note that VL breakup effects explain the anomalous behavior of the samples with the largest layer separation (see Fig. 2). A sharp drop in $B_{\rm rms}(T)$, similar to that observed in our Bi2212 ($d = 3.82$ nm) and Bi2201 ($d = 2.3$ nm) samples, has previously been observed in pristine Bi2212 [22,23], where it was attributed to VL melting at small superfluid densities close to T_c. Both electromagnetic (EM) and Josephson coupling are expected to stabilize the VL in these materials [23,24]. The temperature at which thermal fluctuations break up a VL stabilized solely by EM coupling is given by $T_{\rm EM} = \Phi_0^2\bar{c}/(32k_B\mu_0\pi^2\lambda_{ab}^2)$ [25] (where $\bar{c}$ is the average CuO_2 layer separation), which is constant for each series as $T \rightarrow 0$. We can therefore estimate $T_{\rm EM} \sim 14$ K for Bi2212 and $T_{\rm EM} \sim 10$ K for Bi2201, both in reasonable agreement with the temperatures at which we observe a sharp drop in $B_{\rm rms}(T)$ in the samples with the largest layer spacing. This suggests that the Josephson coupling, which decreases strongly with increasing layer spacing, stabilizes the VL to higher temperature in the samples with smaller layer spacing but is too weak to do so in the two samples with the largest d. This leaves only EM coupling and the observed VL breakup for $T > T_{\rm EM}$.

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