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Magnetic defects in $La_{2-x}Sr_xCuO_{4-\delta}$

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We report the magnetization as a function of magnetic field and temperature for as-grown and doped La_2CuO_4. Two samples of La_2CuO_4 with differing oxygen treatment and a sample of $La_{1.995}Sr_{0.005}CuO_4$ exhibited T_N of 225, 240, and 215 K, respectively. An anomalous magnetic field dependence of the magnetization was observed above and below T_N for each of these samples, suggestive of the presence of small ferromagnetically coupled domains present within each of these samples. Below T_N these ferromagnetic regions appear antiferromagnetic until application of a critical field switches them to a ferromagnetic domain. Samples of $La_{2-x}Sr_xCuO_4$ with $x=0.05$ and 0.15 show no antiferromagnetic ordering and no anomalous ferromagnetic domains. These anomalous magnetic effects give credence to models of formation of unusual magnetic domains within these antiferromagnetically coupled materials.

The discovery of superconductivity of doped La_2CuO_4 by Bednorz and Müller[1] has stimulated intensive experimental and theoretical study of these and related materials. In order to understand the mechanisms for the novel high-temperature superconductivity, it is important to elucidate the novel phenomena present across the entire range of compositions as a function of doping. It has already been demonstrated that there are unusual two-dimensional (2D) and three-dimensional (3D) antiferromagnetic orderings within the La_2CuO_4 that are extremely sensitive to the tetragonal-to-orthorhombic structural transitions and doping and oxygen deficiencies.[2-8] The temperature dependence of the magnetic susceptibility for La_2CuO_4 and lightly doped La_2CuO_4 reflect the presence of a 3D antiferromagnetic transition near 250 K, T_N depending upon the doping level and oxygen content.[9] Recent neutron diffraction studies of $YBa_2Cu_3O_{6+x}$ with $x=0.0$ and 0.15 confirm the existence of long-range three-dimensional antiferromagnetic ordering in the 1:2:3 compounds as well.[10] These and other experiments have led to the suggestion that the magnetism underlies the origin of the high-temperature superconductivity.[11-19]

We report here the results of an extensive study of the magnetic field and temperature dependence of the magnetization of pure and doped La_2CuO_4. Samples A and B of La_2CuO_4, grown under slightly different conditions, have an antiferromagnetic 3D transition temperature, T_N of 225 and 240 K, respectively. Sample C of composition $La_{1.995}Sr_{0.005}CuO_4$ has $T_N=215$ K. Samples D and F, of composition $La_{1.95}Sr_{0.05}CuO_4$ and $La_{1.85}Sr_{0.15}CuO_4$, respectively, show no indication of bulk antiferromagnetic ordering. Samples with finite T_N displayed an anomalous magnetic behavior not present in samples that had an absence of magnetic ordering. For the former samples, for $T>T_N$, the magnetization M versus magnetic field H studies show a nonlinear behavior consistent with the presence of small ferromagnetically coupled clusters of spin of net moment $\sim 25\mu_B$. Below T_N, the M vs H curves at constant temperature T showed an anomalous increase at a T-dependent H_c. Generally, H_c was ~ 60 kG. This behavior below T_N is in accord with the previously mentioned ferromagnetic domains becoming antiferromagnetically coupled into the surrounding lattice below T_N, and, subsequently, undergoing a transition back to the ferromagnetic state under application of a sufficiently large applied field. These results suggest the importance of local ferromagnetic order around defects in the otherwise antiferromagnetically ordered CuO system.

Samples were grown via the solid-state technique.[20] Sample A of La_2CuO_4 was sintered in oxygen while sample B of La_2CuO_4 was sintered in oxygen at 1000 °C. The Sr-doped samples were prepared using the solid-state processes.[20] The static magnetic susceptibility was measured using powdered samples in a previously described Faraday balance[21,22] that allow measurements to fields of 80 kG.

Figure 1 summarizes the temperature dependence of the magnetic susceptibility for samples A through E, taken at fields of approximately 10 kG. In accord with earlier reports, sample B, sintered in air as opposed to oxygen (sample A), has a slightly higher T_N and a sharper three-dimensional transition. Substitution of 0.005 La with Sr broadens the 3D transition substantially and shifts it to even lower temperature. Substitution of 0.05 La with Sr eliminates the magnetic ordering altogether, and the onset of a substantial bulk superconductivity is observed at low temperatures [for samples of lighter doping and undoped samples, a very small sample (less than 0.0001) of the sample becomes superconducting at low temperatures, consistent with earlier reports[9]]. Increasing the doping level further to form $La_{1.85}Sr_{0.15}CuO_4$ shifts the Pauli susceptibility from that observed for the 0.05-Sr sample but leads to no reappearance of the antiferromagnetic ordering.

The magnetization as a function of applied magnetic field was measured for each of these samples as a function of temperature. Figure 2 presents a summary of represen-

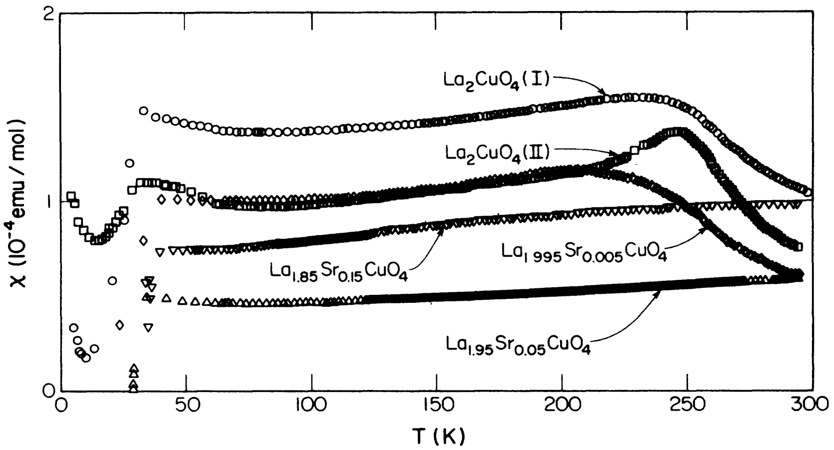

FIG. 1. Magnetic susceptibility vs temperature for samples A: La_2CuO_4; B: La_2CuO_4; C: $La_{1.995}Sr_{0.05}CuO_4$; D: $La_{1.95}Sr_{0.05}CuO_4$; E: $La_{1.85}Sr_{0.15}CuO_4$. Data are corrected for the core diamagnetization (Ref. 30). Data were acquired at fields of ~10.5 kG.

tative data for sample B, La_2CuO_4. At 300 K, the magnetization is linearly proportional to magnetic field as is usual for most materials. As T is lowered toward T_N, the low field ($H < 10$ kG) susceptibility increases while at higher fields ($H > 30$ kG), there is an increasingly obvious sublinearity in M vs H, for example, as seen in the 240 K data indicated in Fig. 2. Decreasing T further to below T_N, the M vs H curves change character. The low-field response continues to follow that illustrated in Fig. 1, while above a critical field, H_c, there is a rapid rise in M as a function of H followed by a linear increase in M vs H at even higher fields. It is noted that the high- and low-field M vs H slopes are nearly identical. For even lower temperatures, this new anomalous M vs H continues to be observed, although the H_c shifts to higher fields with decreasing T, as seen for example at 120 K, Fig. 2. The inset to Fig. 2 shows a typical sliding derivative of M vs H, dM/dH, illustrated with the 120-K data. It is noted that the derivative for $H \gg H_c$ returns to nearly the same value as that for $H \ll H_c$. Very similar behavior was observed for sample A of La_2CuO_4.[23]

A similar series of data taken for sample C, $La_{1.995}$-

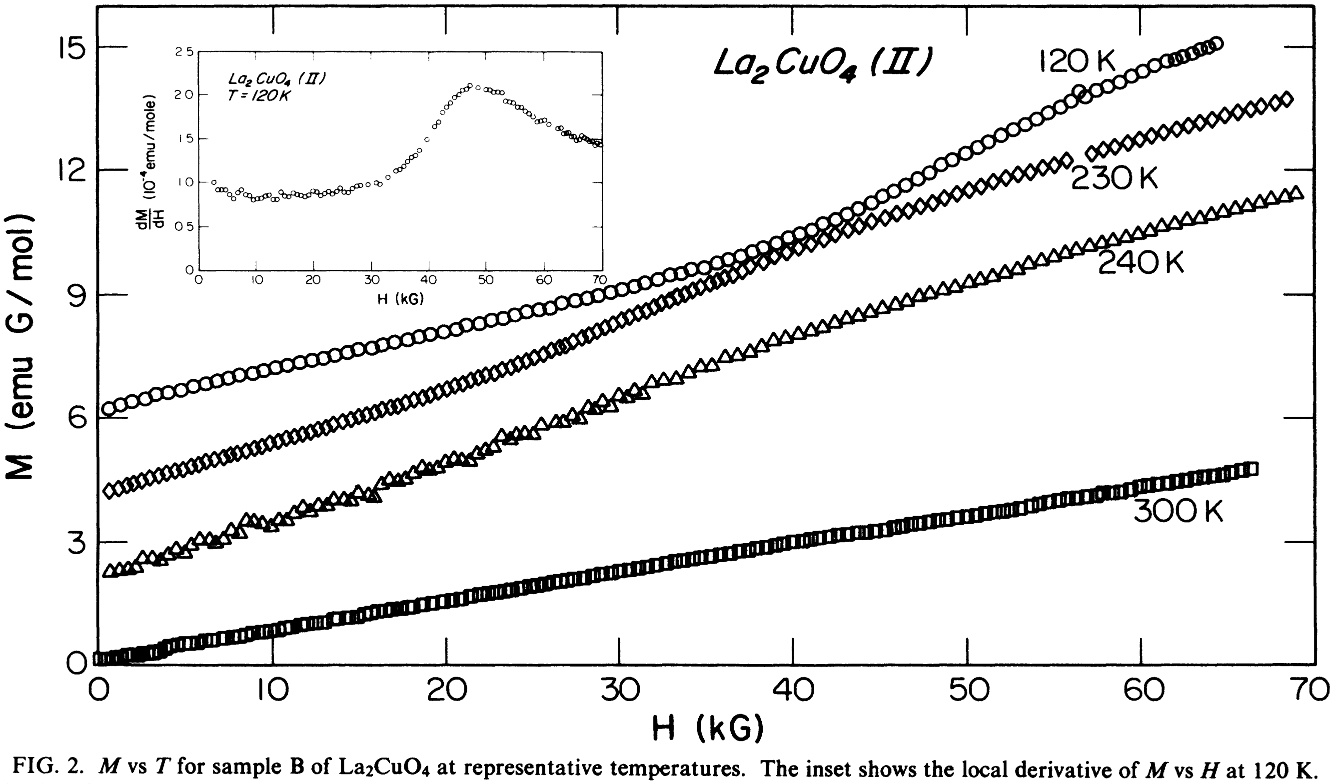

FIG. 2. M vs T for sample B of La_2CuO_4 at representative temperatures. The inset shows the local derivative of M vs H at 120 K. The data for each succeeding curve are displaced by 2 emu G/mol.

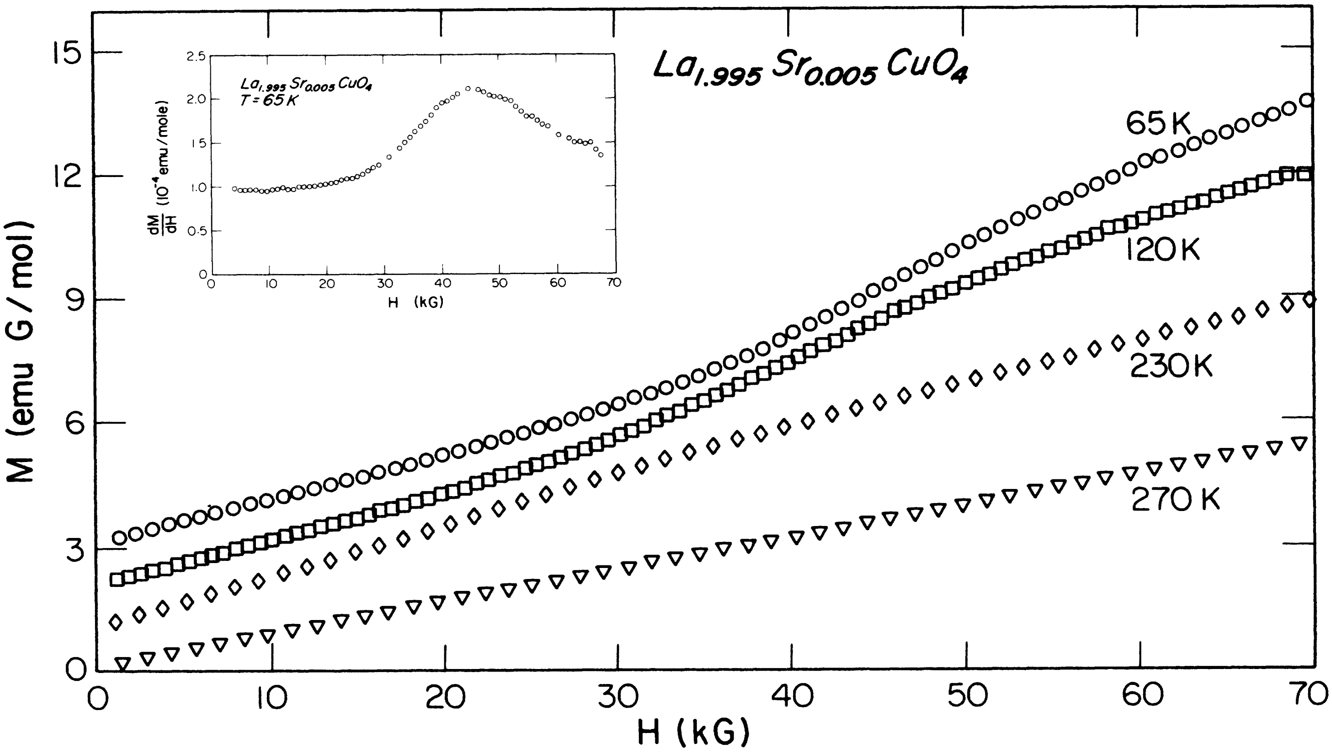

FIG. 3. M vs H at representative temperatures for sample C, $La_{1.995}Sr_{0.005}CuO_4$. The local derivative of M vs H as a function of H is shown in the inset for $T = 65$ K. The data for each succeeding curve are displaced by 2 emu G/mol.

$Sr_{0.005}CuO_4$ is shown in Fig. 3. Despite the more gradual transition to the antiferromagnetic state, a very similar behavior in M vs H as a function of T is observed, with very similar magnitudes for the effect. No significant hysteresis with magnetic field was observed in the behavior for any of the samples A through C. Figure 4 summarizes the T behavior of H_c for samples B and C. In both cases, H_c is meaningless until $T < T_N$. Following a rapid rise in H_c as T decreases below T_N, H_c continues to increase, essentially linearly with decreasing T, with a slope of ~ -0.12 kG/K.

The origins of this anomalous magnetic phenomena in pure and doped La_2CuO_4 are important, especially in the context of the proposals of role of local magnetic ordering in the pairing mechanism for high-temperature superconductivity in these materials. The sublinear behavior of M vs H for $T > T_N$ is reminiscent of the behavior of isolated Curie spins at magnetic fields such that $\mu H \sim k_B T$. For a cluster of spins ferromagnetically coupled to form a moment $NgS\mu_B$, the magnetization is expected to follow a Brillouin function as the applied field is increased. A cluster of ~ 25 ferromagnetically spin-$\frac{1}{2}$ S would begin to show sublinear deviations in their M vs H behavior for the temperatures and magnetic fields used in this experiment. Further decrease T below T_N leads to a change in the M vs H behavior as noted above. The ferromagnetic clusters no longer appear present at low fields. As H is increased at constant T, there is a broad increase in $M(H)$ at H_c similar to a spin flop of an antiferromagnetic region to form a ferromagnetic moment ΔM. The magnitude of ΔM involved in each sample appears independent of T, and corresponds to approximately $\sim(0.02\text{–}0.05)\%$ of the Cu sites becoming ferromagnetically ordered. The magnitude of the ferromagnetic ΔM observed for $H > H_c$ below T_N is the same as that observed for the sublinear dependence with field of the susceptibility above T_N. The persistence of anomalous magnetic behavior to $T > T_N$ argues that the broad anomaly in $M(H)$ at H_c for $T < T_N$ is not a "flop" or canting of all the spins in the ordered antiferromagnetic state.

Spins in the bc plane of La_2CuO_4 tend to order ferromagnetically while there is antiferromagnetic ordering between new planes.[2] It has been suggested[11-19] that there is strong local coupling among spins within the CuO planes. Presence of a single isolated positive hole in the

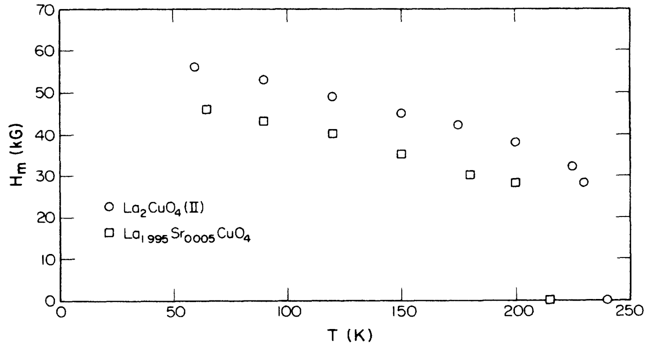

FIG. 4. Variation of H_c vs T for samples B, La_2CuO_4, and sample C, $La_{1.995}Sr_{0.005}CuO_4$.

lattice may lead to polarization of the neighboring spins in a ferromagnetic manner. This would enable greater delocalization of the individual hole. Alternatively, the local defect causing the formation of a ferromagnetic cluster may be a neutral structural defect, for example, an oxygen or copper vacancy. As T is decreased below T_N, the spins on the surface of the ferromagnetic cluster will interact with the antiferromagnetically ordered spin lattice surrounding the cluster. This interaction may be sufficient to drive the local order within the cluster antiferromagnetic as well. Application of a sufficiently large external magnetic field may then drive the cluster ferromagnetic at a critical field H_c. It has been suggested[11-19] that the formation of local ferromagnetic order around individual charge defects may promote pairing into doubly charged bipolarons of dopant-induced holes in the CuO planes. Though dopant-induced[24-26] and photoinduced[27,28] local defects have been reported, and the presence of bipolaron-type defects suggested,[19,29] we do not observe any significant increase in the measured ΔM when our samples are doped with 0.05 or 0.15 Sr.

In summary, we have reported an anomalous magnetic field dependence to the temperature dependence of the magnetization La_2CuO_4, which disappears upon doping to composition such that the antiferromagnetic state is no longer observed. The anomalies reported are consistent with the presence of a small number of ferromagnetically coupled domains of spins which become antiferromagnetically coupled into the surrounding lattice below T_N. Upon application of fields greater than H_c, these localized domains undergo a transition back to the ferromagnetic state. The presence of these magnetic defects with the absence of any significant change in their number due to Sr doping is important for the understanding of the pairing mechanisms relevant for this class of high-temperature superconducting materials.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsom, C. R. Safinya, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).

[3] K. Yamada, E. Kudo, Y. Endoh, Y. Hidaka, M. Suzuki, and T. Murakami, Solid State Commun. (to be published).

[4] G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Kastner, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, Phys. Rev. Lett. **59**, 1613 (1987).

[5] Y. J. Uemura *et al.*, Phys. Rev. Lett. **59**, 1045 (1987).

[6] D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, Phys. Rev. B **36**, 4007 (1987).

[7] T. Freltoft, J. P. Remeika, D. E. Moncton, A. S. Cooper, J. E. Fischer, D. Harshman, G. Shirane, S. K. Sinha, and D. Vaknin, Phys. Rev. B **36**, 826 (1987).

[8] J. Endoh, K. Yamada, R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. R. Thurston, J. M. Tranquada, G. Shirane, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki, and T. Murakami (unpublished).

[9] R. L. Greene, H. Maletta, T. S. Plaskett, J. G. Bednorz, and K. A. Müller, Solid State Commun. **63**, 379 (1987).

[10] J. M. Tranquada, D. E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston, Phys. Rev. Lett. **60**, 156 (1988).

[11] P. W. Anderson, Science **235**, 1196 (1987).

[12] P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).

[13] V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[14] P. A. Lee and M. Read, Phys. Rev. Lett. **58**, 2691 (1987).

[15] J. E. Hirsch, Phys. Rev. Lett. **59**, 228 (1987).

[16] S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna, Phys. Rev. B **35**, 8865 (1987).

[17] D. J. Thouless, Phys. Rev. B **36**, 7187 (1987).

[18] Y. Hasegawa and H. Fukayama, Jpn. J. Appl. Phys. **26**, L322 (1987).

[19] J. R. Schrieffer, X.-G. Wen, and S.-C. Zhang, Phys. Rev. Lett. **60**, 944 (1988).

[20] X. D. Chen, S. Y. Lee, M. P. Golben, S. I. Lee, R. D. Mcmichael, Y. Song, T. W. Noh, and J. R. Gaines, Rev. Sci. Instrum. **58**, 1565 (1987).

[21] F. Zuo, B. R. Patton, T. W. Noh, S.-I. Lee, Y. Song, J. P. Golben, X.-D. Chen, S. Y. Lee, J. R. Gaines, J. C. Garland, and A. J. Epstein, Solid State Commun. **64**, 83 (1987).

[22] F. Zuo, B. R. Patton, D. L. Cox, S. I. Lee, Y. Song, J. P. Golben, X. D. Chen, S. Y. Lee, Y. Cao, Y. Lu, J. R. Gaines, J. C. Garland, and A. J. Epstein, Phys. Rev. B **36**, 3603 (1987).

[23] Examination of the data in Ref. 8 suggests the universality of the phenomena as indications of similar features are present in the limited data presented there for La_2CuO_4.

[24] S. L. Herr, K. Kamarás, C. D. Porter, M. G. Doss, D. B. Tanner, D. A. Bonn, J. E. Greedan, C. V. Stager, and T. Timusk, Phys. Rev. B **36**, 733 (1987).

[25] S. Etemad, D. E. Aspnes, M. K. Kelly, R. Thompson, J.-M. Tarascon, and G. W. Hull (unpublished).

[26] T. Koide, H. Fukutani, A. Fujimor, R. Suzuki, T. Shidara, T. Takahashi, S. Hosoya, and M. Sato, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

[27] Y. H. Kim, A. J. Heeger, L. Acedo, G. Stucky, and F. Wudl, Phys. Rev. B **36**, 7252 (1987).

[28] J. M. Ginder, M. G. Roe, Y. Song, R. P. McCall, J. R. Gaines, E. Ehrenfreund, and A. J. Epstein, Phys. Rev. B **37**, 7506 (1988).

[29] M. J. Rice and S. Jeyadev, Synth. Met. **22**, 209 (1988).

[30] The core diamagnetization in units of 10^{-6} emu/g ion utilized were La^{3+}: -20; Sr^{2+}: -15; Cu^{+}: -12; O^{2-}: -12. Values are from L. M. Mulay and E. P. Boudreaux, *Theory and Application of Molecular Diamagnetization* (Wiley, New York, 1976), p. 306.