PHYSICAL REVIEW B VOLUME 58, NUMBER 14 1 OCTOBER 1998-II

Superconductivity in the Mg-doped $CuBa_2Ca_3Cu_4O_{12-y}$ system

S. K. Agarwal,* A. Iyo, K. Tokiwa,† Y. Tanaka, K. Tanaka,† M. Tokumoto, N. Terada, T. Saya, M. Umeda, and H. Ihara
Electrotechnical Laboratory, 1-1-4, Umezono, Tsukuba, Ibaraki 305, Japan

M. Hamao and T. Watanabe
Department of Applied Electronics, Science University of Tokyo, Chiba, Noda 278, Japan

A. V. Narlikar
Superconductivity Division, National Physical Laboratory, K.S. Krishnan Road, New Delhi-110012, India

(Received 22 December 1997)

Synthesis of $CuBa_2Ca_3Cu_4O_{12-y}$ (Cu-1234) with Mg doping at the Ca sites, hitherto unexplored, is attempted and reported here. Different samples with 5%, 10%, 20%, and 33% Mg (in nominal stoichiometry) have been prepared in gold capsules under 3.5 GPa pressure and at about 1000 °C temperature using a cubic anvil-type high-pressure machine. The samples were characterized through x-ray diffractometry, resistivity, dc susceptibility, and Hall effect measurements. The samples were then aligned along their c axis under 10 T field at room temperature. Magnetization (both in $H\|ab$ and $H\|c$) was measured between 120 and 5 K in different field values up to 5 T. The superconducting anisotropy (defined as $\xi_{ab}/\xi_c = H_{c2}^{ab}/H_{c2}^{c}$), estimated in the reversible magnetization regime, comes out to be about 1.4, and is lower than that of the pristine sample. Improvement in the anisotropy factor obtained has been discussed in light of the observed changes in the lattice parameters and the hole concentration, emanating from Mg doping in the Cu-site vacancies in charge reservoir blocks of the 1234 structure. [S0163-1829(98)07538-9]

I. INTRODUCTION

The emergence of the Hg-based 136 K high-temperature cuprate superconductor (HTSC) and its T_c enhancement of 156 K has sparked off hectic activity in this area. Since then many other systems like TlBaCaCuO, (Cu-Tl)BaCaCuO having a cationic stoichiometry of 1223 and 1234, have been generated[1–3] to yield a T_c of around 120 K. Most notably among them is the $n=4$ member of the $CuBa_2Ca_{n-1}Cu_nO_{12-y}$ family. Besides possessing high critical temperature T_c, high critical current density J_c, and high irreversibility field H_{irr}, this happens to be the only HTSC material without any toxic components like Hg or Tl.[4–8] $CuBa_2Ca_3Cu_4O_{12-y}$ (Cu-1234) is a high-pressure–high-temperature phase exhibiting superconductivity at 118 K at ambient pressure. Superconducting anisotropy for this compound is also the least among such HTSC families. Such low anisotropy has its root in the crystal structure of this compound itself. Here the superconducting blocks of $Ca_3Cu_4O_8$ are separated by the conducting $CuBa_2O_{4-y}$ charge reservoir blocks instead of the nonconducting $TlBa_2O_3$ blocks in the analogous Tl-1234 superconductor.[5–7] The low anisotropy has been thought to be strongly related to the short superconducting coupling between such blocks mediated by the conducting (possibly superconducting) charge reservoir layers. Such a coexistence of low superconducting anisotropy and high critical temperature T_c is not contradictory in such materials and has already been considered by Ihara *et al.*[9]

From the studies on (Cu, C)-1234 by Iyo *et al.*[10] and the crystal structure refinement studies carried out on small crystals of Cu_x-1234 and (Cu_xC_{1-x})-1234 and its higher homologues by Akimoto *et al.*,[11] it is concluded that the Cu-site nonstoichiometry in $Cu_xBa_2Ca_{n-1}Cu_nO_y$ compounds and the presence of the CO_3 group in the $Cu_xC_{1-x}Ba_2Ca_{n-1}Cu_nO_y$ mainly affect the thickness of the charge reservoir layer and the thickness of the superconducting block is maintained as a similar structural and electrical environment. It is therefore thought in this scenario that Mg occupying the vacant sites in the charge reservoir layers and the Ca sites in the superconducting block would have the desired effect of better inter-block coupling of the $Ca_3Cu_4O_8$ blocks leading to improved superconducting properties.

In this paper we report an investigation of the doping effects of Mg ions in the crystal structure of Cu-1234 and its superconducting properties. The superconducting anisotropy factor and both in- and out-of-plane coherence lengths have been determined through upper critical field measurements on the c-axis aligned samples. The ensuing results have been discussed in the light of the observed changes in the lattice parameters and the hole density of the samples.

II. EXPERIMENTAL DETAILS

Samples with the nominal composition of $CuBa_2(Ca_{1-x}Mg_x)_3Cu_4O_{12-y}$ ($x=0.05$, 0.10, 0.20, and 0.33) have been synthesized through the solid-state reaction route with appropriate precursors. The precursors were prepared by calcining the well ground mixtures of $BaCO_3$, $CaCO_3$, CuO, and MgO (with purity >99.9%) in flowing oxygen for a total span of 72 h with intermediate grindings

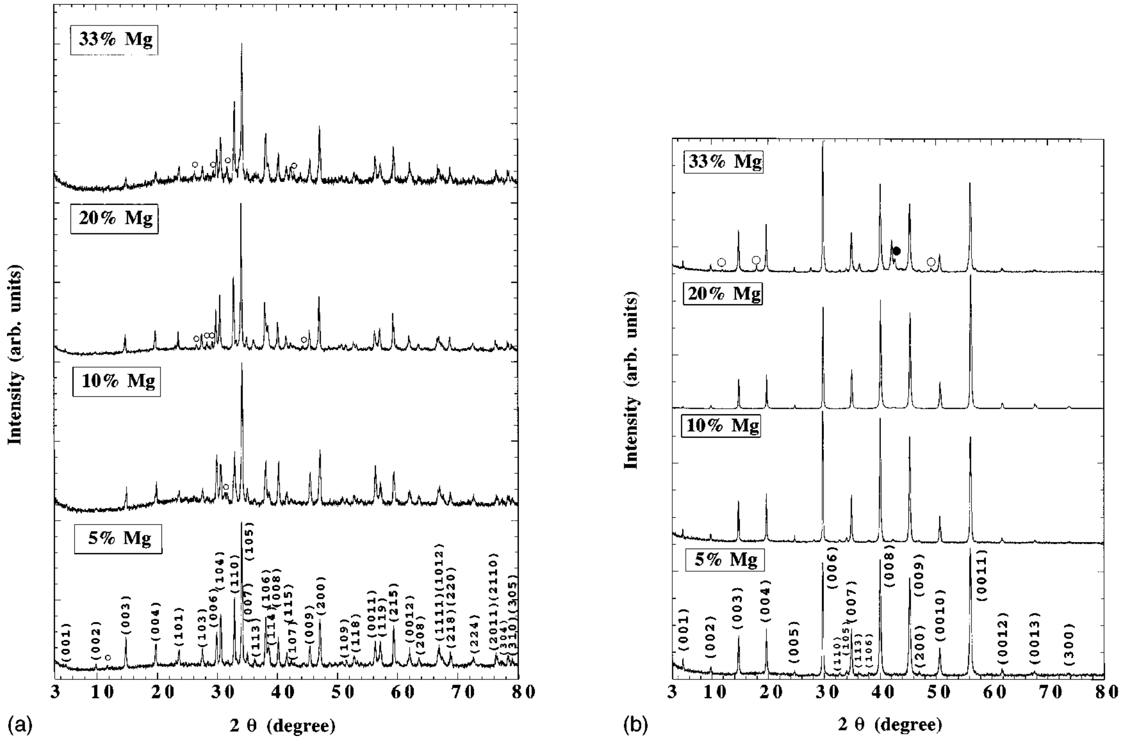

FIG. 1. (a) X-ray diffractograms of various Mg-doped Cu-1234 unaligned samples. ○ refers to unidentified phase. (b) X-ray diffractograms of various Mg-doped Cu-1234 aligned samples. ○ refers to unidentified phase.

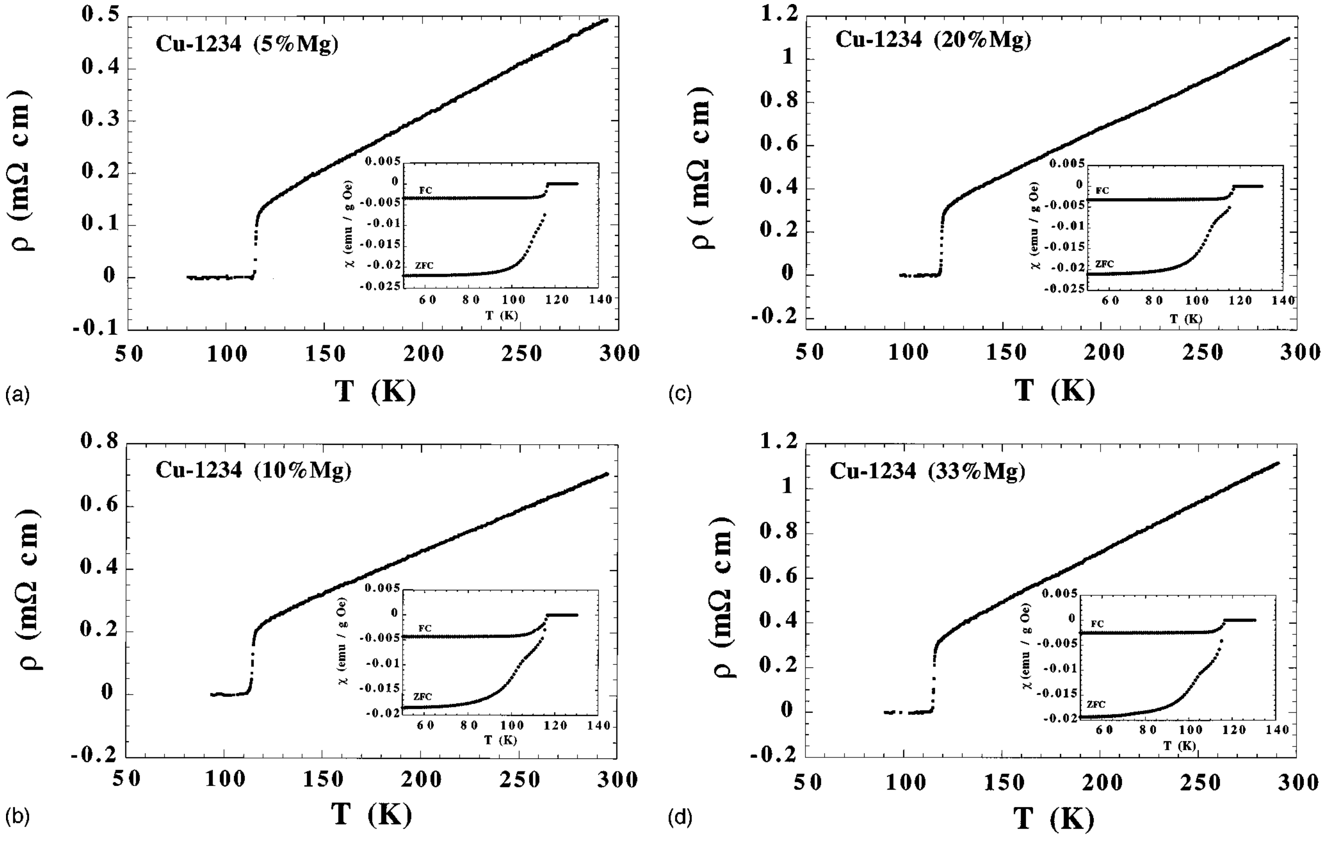

FIG. 2. (a)–(d) Resistivity behavior with temperature. Inset shows the diamagnetic transition.

TABLE I. Lattice parameters, carrier concentration, and superconducting parameters for pure and Mg-doped Cu-1234 samples.

Sample	T_c (K)	a (Å)	c (Å)	$1/eR_H$ ($10^{21}/\mathrm{cm}^3$)	n_H ($/\mathrm{CuO}_2$)	$H_{c_2}^{ab}(0)$ (T)	$H_{c_2}^{c}(0)$ (T)	ξ_{ab} (Å)	ξ_c (Å)	ξ_{ab}/ξ_c
Cu-1234	117.5	3.856	17.993	5.40	0.36	195	121	16	10	1.6
5% Mg ($x=0.05$)	116.6	3.855	17.954	7.61	0.50	127	86	19	13.2	1.46
10% Mg ($x=0.10$)	116.4	3.848	17.907	7.05	0.47	103	74	20	14.2	1.41
20% Mg ($x=0.20$)	116.8	3.848	17.907	7.86	0.53	115	80	20	14	1.43
33% Mg ($x=0.33$)	116.6	3.847	17.917	5.19	0.34	110	79	20	14.5	1.38

Standard deviation in $a=0.000\,24$ Å.
Standard deviation in $c=0.001\,63$ Å.

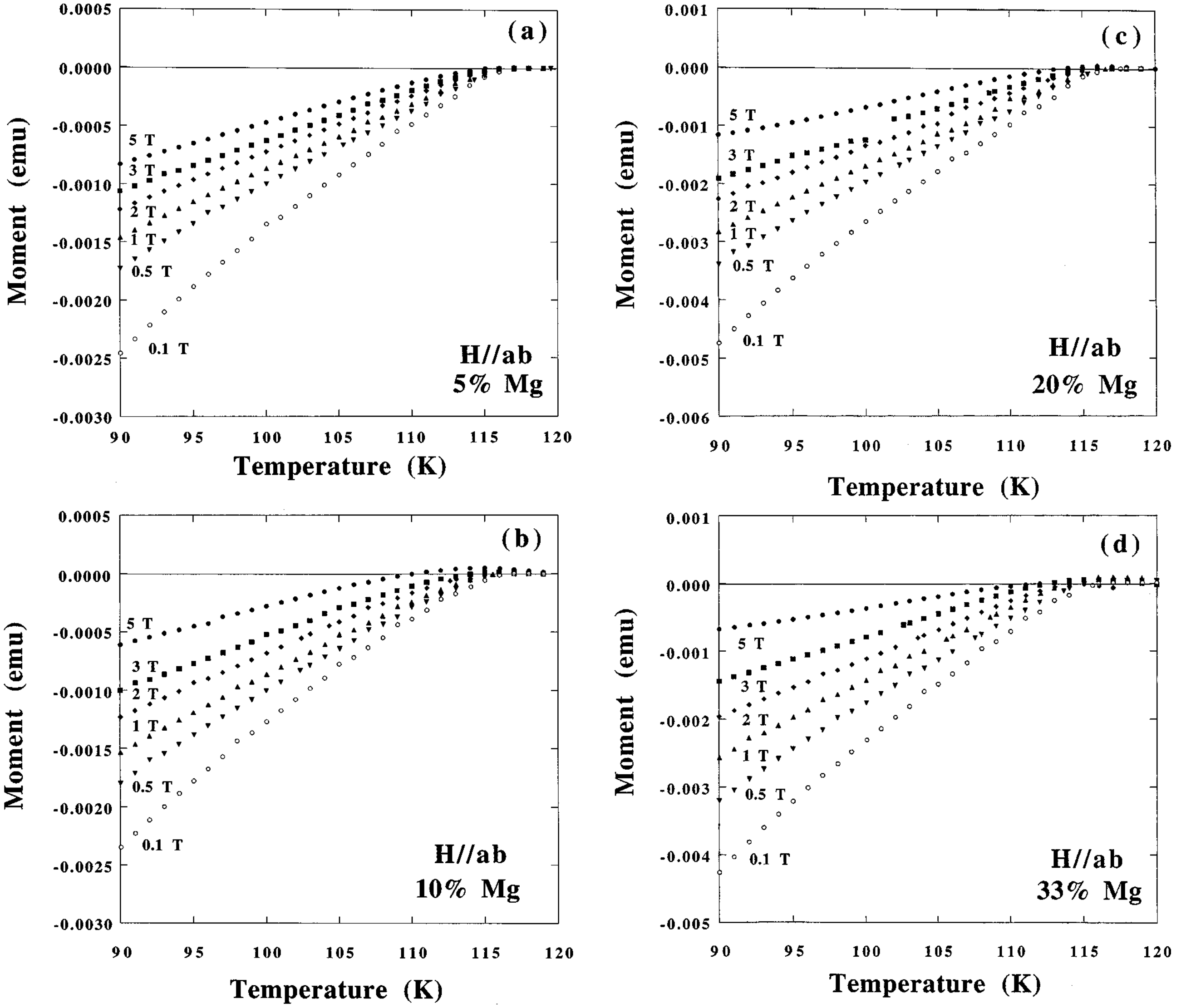

FIG. 3. (a)–(d) Magnetization-temperature behavior for different field values in $H//ab$ configuration.

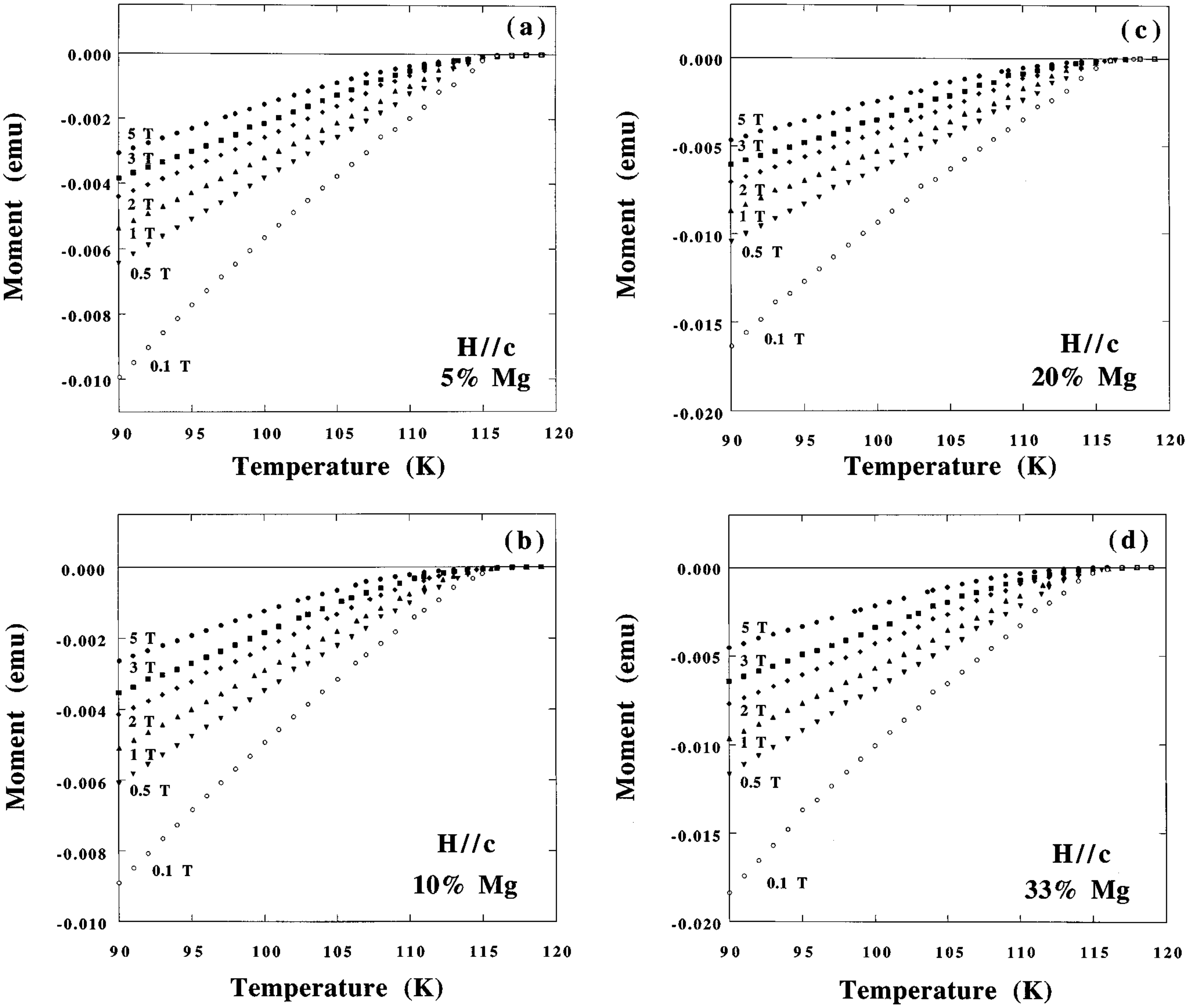

FIG. 4. (a)–(d) Magnetization-temperature behavior for different field values in $H//c$ configuration.

for powder homogeneity. The precursors were mixed with small amounts of AgO (0.4 mol fraction) as oxidizer and $AgCO_3$ (0.2 mol fraction) for Cu-1234 phase stabilization. The final reaction to realize the 1234 material was carried out at 1000 °C in a gold capsule at 3.5 GPa pressure in a cubic anvil-type high-pressure machine (Riken CAP-07). The sample was subsequently quenched to ambient temperature before the pressure was released.[12] It is worth pointing out here that even though a very small amount of $AgCO_3$ has been added to the precursor before the high-pressure treatment, the final 1234 material realized is not devoid of the oxycarbonate content, however small its fraction may be.

Powder x-ray diffraction (XRD) analysis of the samples was carried out using a Rigaku RINT 1000 diffractometer with monochromatized Cu K_α radiation. These samples were further characterized for their superconductivity through resistivity (four-probe technique) and dc susceptibility measurements (Quantum Design MPMS SQUID magnetometer). Finely ground powders of these materials were mixed with an epoxy resin (Cemedine EP-007) in a teflon tube and aligned along the c axis in a field of 10 T for 10 h at room temperature using the anisotropic normal-state magnetic susceptibility. The degree of c-axis alignment is checked through the intensities of the tetragonal $(00l)$ peaks of the diffractograms. Hall coefficient measurements on the unaligned samples have also been carried out in 2 T field in the temperature range 300–120 K, to check for the possible variation in the hole concentration resulting from Mg doping.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the XRD patterns of both the as-prepared randomly oriented and c-axis aligned samples with different Mg contents. All the characteristic peaks corresponding to an average tetragonal 1234 structure with $P4/mmm$ symmetry could be identified with some unidentified minor impurity peaks. A small peak (marked ●) corresponding to MgO was also seen in the highest doped

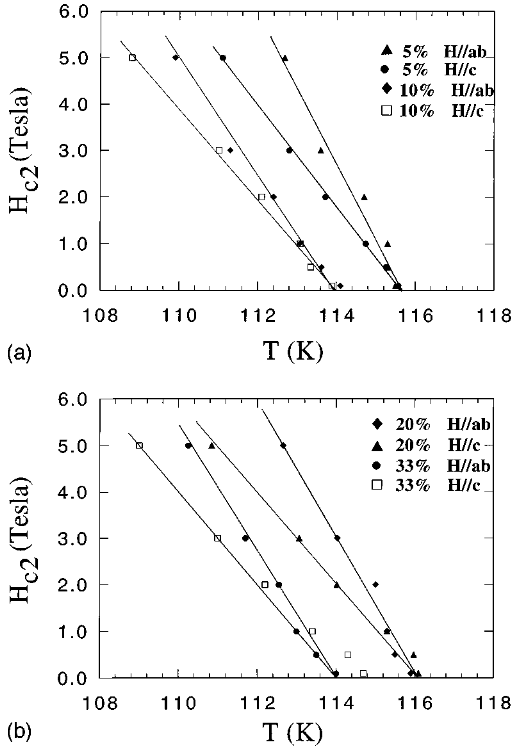

FIG. 5. (a) Temperature dependence of H_{c2} for 5% and 10% Mg ($x=0.05$ and 0.10) doped samples in $H//ab$ and $H//c$ configurations. (b) Temperature dependence of H_{c2} for 20% and 33% Mg ($x=0.20$ and 0.33) doped samples in $H//ab$ and $H//c$ configurations.

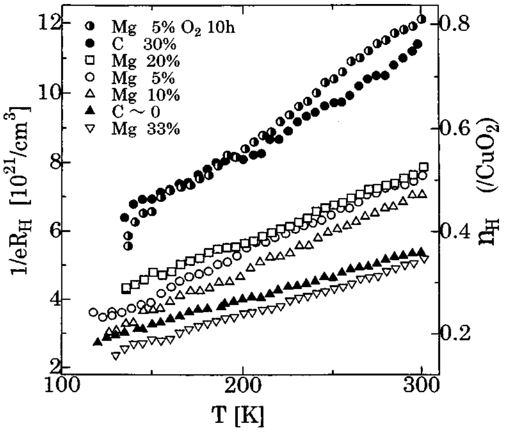

FIG. 6. Temperature dependence of $(1/eR_H)$ and the hole number $n_H(/\mathrm{CuO_2})$.

(33% Mg) sample. While there is not much change in the *a*-axis parameter with increasing Mg content (0.02 Å), a noticeable reduction in the *c* parameter (0.07 Å) has been observed till $x=0.10$ (10% Mg), beyond which it remains nearly constant. The degree of *c*-axis alignment of the doped samples was checked through the equation $P(006)=1-\beta$, where

$$\beta=(I_{105}/I_{006})^{\text{aligned}}/(I_{105}/I_{006})^{\text{unaligned}}$$

and I_{105} and I_{006} are the relative intensities of the (105) and (006) reflections.[13] The *c*-axis alignment was seen to be better than 98% in all the Mg-doped samples.

The resistivity-temperature behavior of the various Mg-containing samples is provided in the Figs. 2(a)–2(d). All the samples exhibit good metallicity with resistivity zero temperature around 116 K, closely matching with $T_c(R=0)=117.5\,\mathrm{K}$ of the undoped Cu-1234 material. The diamagnetic susceptibility measurements with 10 Oe field also corroborate these transition temperatures and are shown in the insets of their respective figures. Phase purity of the materials is also indicated by the well-defined single diamagnetic transition.

The superconducting anisotropy of the cuprate superconductors is seen to be related to the anisotropy in their upper and lower critical fields H_{c2} and H_{c1}, coherence length ξ, and the field penetration depth λ. The anisotropy parameter γ has been defined as[14] $\gamma=H_{c2}^{ab}/H_{c2}^{c}=\xi_{ab}/\xi_c$. dc magnetization on the *c*-axis aligned samples was measured from 120 to 5 K under several field values ranging from 0.1 to 5 T. Figs. 3(a)–3(d) and Figs. 4(a)–4(d) depict the magnetization data for the $H//ab$ and $H//c$ configurations, respectively, for the various Mg-doped samples. A linear extrapolation of the magnetization in reversible regime to the normal-state phase line gives the relationship between T_c and H_{c2}. Figures 5(a) and 5(b) give the temperature dependence of H_{c2}^{ab} and H_{c2}^{c} for samples with 5%, 10% Mg ($x=0.05$ and 0.10) and for 20%, 33% Mg ($x=0.20$ and 0.33) dopings, respectively. The upper critical fields are estimated through an extrapolation to $T=0$ using the Werthamer-Helfand-Hohenberg (WHH) relation[15] $H_{c2}(0)=-0.69\,(dH_{c2}/dT)_{T_c}T_c$. Table I lists the values of $H_{c2}^{ab}(0)$ and $H_{c2}^{c}(0)$ for the different samples and are compared with those of the pristine sample. The superconducting anisotropy factor γ as determined through the ratio of $H_{c2}^{ab}(0)/H_{c2}^{c}(0)$ comes out to be of the order of 1.4, indicating a clear improvement over that of the undoped sample.

Recently, Iyo *et al.*[10] have reported that the *c* parameter decreased with increase of the carbon content in the $(\mathrm{Cu}_x\mathrm{C}_{1-x})$-1234 from 18.02 Å for $x=1$ to 17.90 Å for the $x=0.5$. Akimoto *et al.*[11] have carried out further investigations on the crystal chemistry of small crystals of the compounds belonging to the $\mathrm{Cu}_x\mathrm{Ba}_2\mathrm{Ca}_{n-1}\mathrm{Cu}_n\mathrm{O}_y$ and $\mathrm{Cu}_x\mathrm{C}_{1-x}\mathrm{Ba}_2\mathrm{Ca}_{n-1}\mathrm{Cu}_n\mathrm{O}_y$ families with $n=4,5,6$. It was concluded that with increasing *x* in the carbonless case, the *c* parameter decreases. And in the Cu-C case, the Cu content *x* decreases together with decrease in the *c* parameter. More significantly, the thickness of the charge reservoir block (CRB) decreases with increasing Cu-site occupancy in the carbonless case and with increasing C content in the (Cu-C) case, while the superconducting layer block (SLB) thickness remained unchanged in both the families with $n=4$ and the higher homologues of $n=5$ and 6. The decrease in the *c* parameter leading to a shrinkage of the CRB is the general scenario where no substitution in SLB is attempted. The present case of Mg incorporation is seemingly such an extension. The *c* parameter would be expected to reduce in both situations of Mg occupying defect sites (Cu-site vacancies) in the charge reservoir layer and at the perovskite Ca sites in the superconducting block. Even though Mg substitution at the perovskite Y or Ca sites[16,17] has been reported in the case of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ and $\mathrm{Bi_2Sr_2CaCu_2O_y}$, the observed decrease in the hole density with increase in Mg content in the present case (Fig. 6 and Table I) is the obvious signature of Mg at the defect sites of CRB and is the most likely situation. The intersuperconducting block coupling, therefore, is expected to be modified favorably as a result of the decrease in the CRB thickness in spite of the fact that such a blocking layer has been rendered less conducting. CRB seemingly resembles the proximity type of a superconductor–normal-metal–superconductor junction (SNS) with the reduction of its size overcompensating the decrease in carrier density. In such a situation, superconducting wave functions of the adjoining SLB would have a better overlap, leading eventually to a less superconducting anisotropy as observed presently.

It is interesting to note from Fig. 6 that the hole concentration in the various Mg-doped samples lies in the limits of that of 0% and 30% carbon content 1234 samples, with the oxygenated 5% Mg sample having a high hole density as that of the 30% carbon case, while 0% carbon, 33% Mg cases correspond to nearly the same lower hole density. Apparently, Mg ions seem to have a stronger affinity to occupy the vacancies in the charge reservoir layer than carbon, at least in the present heat treatment schedule, making the CRB less conducting. The observed increase in the normal-state resistivity (Fig. 2) with increasing dopant content is a clear manifestation of such an effect. The exact mechanism of how the hole density increases with oxygenation (5% Mg), however, is far from clear. It would therefore be worthwhile to determine the hole concentration of the different Mg-doped oxygenated samples and the ensuing effect on the superconducting anisotropy to generate a possible relationship between them.

IV. CONCLUSIONS

Samples with 5% to 33% Mg ($x=0.05$ to 0.33) at Ca in the nominal composition of $CuBa_2(Ca_{1-x}Mg_x)_3Cu_4O_{12-y}$ HTSC material have been synthesized in Au capsules by a high-pressure (3.5 GPa)–high-temperature (1000 °C) reaction process using a cubic anvil-type high-pressure machine. Both a- and c-axis lattice parameters are seen to decrease with Mg incorporation. Hole concentration n_H (as determined through Hall measurements) also decreases from 0.5 to 0.34 per CuO_2 layer for the highest doped sample. The superconducting anisotropy ξ_{ab}/ξ_c of 1.4 as determined by the ratio of upper critical field measurements (through magnetization in $H//ab$ and $H//c$) in the c-axis aligned samples shows an improvement over that (1.6) of the pristine Cu-1234 material and happens to be the least among such families of HTSC's. Such a situation is understood in terms of Mg doping in the charge reservoir blocks (making n_H lower and reducing the c parameter). The reduction in the intersuperconducting $Ca_3Cu_4O_8$ block spacing (shrinkage of the charge reservoir block thickness) perhaps leads to an enhanced superconducting coupling among them, eventually reducing the anisotropy in these materials.

ACKNOWLEDGMENTS

The authors would like to thank Dr. K. Arai and Dr. H. Simizu of ETL for their interest and encouragement of this work. One of us (SKA) acknowledges the support of INSA-JSPS and STA for the Research Award.

---

*Permanent address: Superconductivity Division, National Physical Laboratory, K.S. Krishnan Road, New Delhi-110012, India.

†Permanent address: Dept. of Applied Physics, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162, Japan.

[1] H. Ihara, K. Tokiwa, H. Ozawa, M. Hirabayashi, A. Negishi, H. Matsuhata, and Y. S. Song, Jpn. J. Appl. Phys., Part 2 **33**, L503 (1994).

[2] M. A. Alario-Franco, C. Chaillout, J. J. Capponi, J. L. Tholence, and B. Souletie, Physica C **222**, 52 (1994).

[3] C. Q. Jin, S. Adachi, X. J. Wu, H. Yamauchi, and S. Tanaka, Physica C **223**, 238 (1994).

[4] H. Ihara, K. Tokiwa, A. Iyo, M. Hirabayashi, N. Terada, M. Tokumoto, and Y. S. Song, Physica C **235–240**, 981 (1994).

[5] H. Ihara, A. Iyo, K. Tokiwa, N. Terada, M. Tokumoto, and M. Umeda, in *Advances in Superconductivity VIII*, edited by H. Hayakawa and Y. Enomoto (Springer-Verlag, Tokyo, 1996), p. 247.

[6] H. Ihara, R. Sugise, M. Hirabayashi, N. Terada, M. Jo, K. Hayashi, A. Negishi, M. Tokumoto, Y. Kimura, and T. Shimomura, Nature (London) **334**, 510 (1988).

[7] H. Ihara, R. Sugise, K. Hayashi, N. Terada, M. Jo, M. Hirabayashi, A. Negishi, A. Atoda, H. Oyanagi, M. Tokumoto, T. Shimomura, and S. Ohashi, Phys. Rev. B **38**, 11 952 (1988).

[8] H. Kumakura, K. Tagana, K. Kawashima, and E. Takayama-Muromachi, Physica C **226**, 222 (1994).

[9] H. Ihara, A. Iyo, K. Tanaka, K. Tokiwa, K. Ishida, N. Terada, M. Tokumoto, Y. Sekita, T. Tsukamoto, T. Watanabe, and M. Umeda, Physica C **282–287**, 1973 (1997).

[10] A. Iyo, K. Tokiwa, N. Terada, M. Tokumoto, M. Hirabayashi, and H. Ihara, in *Advances in Superconductivity VIII* (Ref. 5), p. 289.

[11] J. Akimoto, K. Tokiwa, A. Iyo, H. Ihara, H. Hayakawa, Y. Gotoh, and Y. Oosawa, Physica C **279**, 191 (1997).

[12] A. Iyo, K. Tokiwa, T. Kanehira, H. Ozawa, N. Kobayashi, N. Terada, M. Tokumoto, M. Hirabayashi, and H. Ihara, in *Advances in Superconductivity VII*, edited by K. Yamafuji and T. Morishita (Springer-Verlag, Tokyo, 1995), p. 825.

[13] H. Ihara, *Advances in Superconductivity VII* (Ref. 12), p. 255.

[14] S. L. Cooper and K. E. Gray, in *Physical Properties of High Temperature Superconductors IV*, edited by D. M. Ginsberg (World Scientific, London, 1994), p. 61.

[15] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).

[16] K. Moroishi, Y. Ogawa, and A. J. Ikushima, Jpn. J. Appl. Phys., Part 2 **27**, L2330 (1988).

[17] A. Y. Khan, M. Mohammad, M. Sahnaz, and S. K. Hasnain, Mod. Phys. Lett. B **5**, 771 (1991).