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Neutron diffraction was used to determine the crystal structure and magnetic ordering pattern of a La_2CuO_4 single crystal, with and without applied magnetic field. A previously unreported, subtle monoclinic distortion of the crystal structure away from the orthorhombic space group $Bmab$ was detected. The distortion is also present in lightly Sr-doped crystals. A refinement of the crystal structure shows that the deviation from orthorhombic symmetry is predominantly determined to drive a continuous reorientation of the copper spins from the orthorhombic b axis to the c axis, directly confirming predictions based on prior magnetoresistance and Raman scattering experiments. A spin-flop transition induced by a c -axis oriented field previously reported for nonstoichiometric La_2CuO_4 is also observed, but the transition field (11.5 T) is significantly larger than that in the previous work.

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I. INTRODUCTION

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is one of the simplest high-temperature superconductors, and there has been a large amount of work on this system since the discovery of high-temperature superconductivity. Some of the most incisive information has come from neutron scattering, which has provided a detailed microscopic picture of the evolution of the structural and magnetic properties as a function of doping.¹ The parent compound of this family, undoped La_2CuO_4 , is a Mott insulator that orders antiferromagnetically with a Néel temperature, T_N , of approximately 325 K.² Antiferromagnetic long-range order vanishes for $x \approx 0.02$ and is replaced by phases with short-range magnetic order that partially coexist with superconductivity. Neutron scattering data on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have provided the major impetus and motivation for one of the most prominent microscopic models of high-temperature superconductivity, according to which superconductivity is seeded in the charge “stripes” that can be either static (in underdoped materials, in particular around the commensurate hole content $x=1/8$), or fluctuating (in optimally doped and overdoped materials).^{1,3}

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ exhibits a tetragonal crystal structure (with space group $I4/mmm$) at high temperatures, which transforms into an orthorhombic structure (with space group $Bmab$) below a transition temperature up to $T_S=520$ K, that strongly depends on doping.⁴⁻⁶ In the orthorhombic phase, macroscopic samples invariably exhibit crystallographic twinning (that is, the formation of micron-scale domains in which the a and b axes in the copper-oxide planes are interchanged), unless the sample is cooled through T_S under uniaxial stress. Most experimental work on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, including almost all neutron scattering work, has thus been performed on twinned samples.

Recent developments call for a reinvestigation of the interplay between the magnetic and structural correlations in untwinned $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. First, the charge dynamics⁷ and the spin susceptibility⁸ of lightly doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ were found to exhibit sizable in-plane anisotropies, possibly as a consequence of stripe formation. A quantitative correlation with the in-plane anisotropy of the spin correlations is desirable. Second, it was recently shown that it is possible to detwin pure and lightly doped La_2CuO_4 crystals by applying a magnetic field at room temperature.⁹ This indicates a magnetostructural coupling mechanism that is thus far not understood. Third, magnetoresistance measurements¹⁰ and Raman scattering¹¹ experiments in high-magnetic fields have indicated a reorientation of the magnetic moments and associated transport anomalies when a magnetic field is applied along the orthorhombic b axis in the copper-oxide layers. These results, as well as corresponding theoretical work,^{12,13} have yielded predictions for the magnetic field dependence of magnetic Bragg reflections observable in neutron scattering experiments. These predictions partially contradict earlier work.¹⁴

Motivated by these results, we have studied the crystal and magnetic structure of an untwinned La_2CuO_4 single crystal by neutron diffraction. We find a previously unknown, subtle monoclinic distortion of the crystal structure resulting predominantly from displacements of the apical oxygen atoms. This distortion is also present in lightly Sr-doped La_2CuO_4 and may thus be relevant for a complete understanding of stripe formation and charge transport in this system. We also find two magnetic field-induced spin reorientation transitions. When the field is applied along the c axis, we reproduce a previously observed¹⁵ spin-flop transition, albeit at a significantly higher field than that reported earlier. An in-plane magnetic field induces a gradual reorien-

tation of the magnetic moments from the b to the c axis. This confirms the predictions made on the basis of the Raman scattering and magnetoresistance work.^{10–12}

II. EXPERIMENTAL DETAILS

High-quality single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ were grown by the traveling-solvent floating-zone technique as described earlier.⁸ For the experiments we used untwinned crystals of La_2CuO_4 , $\text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4$, and $\text{La}_{1.97}\text{Sr}_{0.03}\text{CuO}_4$ with dimensions $1.45 \times 1.45 \times 2.60 \text{ mm}^3$, $2.10 \times 1.80 \times 2.75 \text{ mm}^3$, and $1.60 \times 2.10 \times 2.55 \text{ mm}^3$, respectively.

Neutron diffraction experiments were carried out on the four-circle diffractometer E5 at the BER II reactor of the Hahn-Meitner-Institut in Berlin. This instrument uses Cu and pyrolytic graphite (PG) monochromators selecting the neutron wavelengths 0.884 \AA and 2.39 \AA , respectively. The samples were placed in a strain-free mount inside a closed-cycle He cryostat. The data were collected with a two-dimensional position sensitive ^3He -detector, $90 \times 90 \text{ mm}$ (32×32 pixels). The refinements of the crystal and magnetic structures were carried out with the programs XTAL 3.4 and FULLPROF, respectively.^{16,17} Here the nuclear scattering lengths $b(\text{O})=5.805 \text{ fm}$, $b(\text{Cu})=7.718 \text{ fm}$, $b(\text{Sr})=7.02 \text{ fm}$, and $b(\text{La})=8.24 \text{ fm}$ were used.¹⁸ For the determination of the magnetic order of the copper sublattice, the magnetic form factor of the Cu^{2+} ion was taken from Ref. 19.

Elastic neutron scattering experiments in magnetic fields up to 14.5 T were performed in a vertical-field cryomagnet installed at the two-axis diffractometer E4 at the Hahn-Meitner-Institut. A PG monochromator working with the (002) reflection was used to select an incident wavelength of 2.44 \AA . In order to reduce the contributions from second-order Bragg reflections, a PG filter was placed into the neutron beam.

In a further effort to clarify the evidence of a fine splitting of reflections resulting in a lower lattice symmetry of La_2CuO_4 high-resolution powder diffraction studies using synchrotron radiation were performed. The experiments were carried out with the high-resolution powder diffractometer on the BM1B (Swiss-Norwegian) beam line at the European Synchrotron Research Facility (ESRF) with photon wavelength 0.5200 \AA . The sample was filled into a 0.5 mm diameter capillary and it was cooled with a cryostream nitrogen cooling system. A complete powder pattern with a 2θ range between 1° and 55° was collected at 100 K . The Rietveld refinements of the powder diffraction data were carried out with the program FULLPROF.¹⁷

The degree of twinning in the crystals was determined by neutron diffraction from the ratios of the intensities of the reflections $h0l$ and $0kl$. As we will discuss in Sec. III A, the reflections $0kl$ in the orthorhombic ($Bmab$) and in the monoclinic ($B2/m$) structure are limited to those for which l is an even number, whereas the reflections $h0l$ are systematically absent with any odd number. The ratio $I(h0l)/I(0kl)$, where h is an odd and l an even number, therefore describes the degree of twinning. The relatively strong reflections 032 and 052 are well suited for this purpose. In the case of La_2CuO_4 the small ratio of 0.006 showed that the crystal is almost

completely detwinned. In contrast, for $\text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4$ and $\text{La}_{1.97}\text{Sr}_{0.03}\text{CuO}_4$, ratios of about 0.10 were found, indicating that the crystals are partially twinned.

III. RESULTS AND DISCUSSION

A. Crystal structure

In order to refine the crystal structure of La_2CuO_4 , a data set with a total number of 1024 (481 unique) reflections was collected at 325 K [that is, above the Néel temperature of this sample $T_N=316(2) \text{ K}$]. Refinements were carried out initially in the orthorhombic space group $Bmab$ ($B 2/m 2_1/a 2/b$). For the extinction correction the formalism of Zachariasen (type I) was used. The refineable parameter g in this formalism is related to the mosaic distribution, and the refinement resulted in the value $g=608(3) \text{ rad}^{-1}$. For the absorption correction, the absorption coefficient $\mu=0.0734 \text{ mm}^{-1}$ was used. The refinement of the overall scale factor as well as the positional and anisotropic thermal parameters resulted in a residual $R_F=0.019$ ($R_w=0.021$). Additionally the occupancies of the different atoms were refined, where the overall scale factor, the g value, the positional parameters, and the temperature factors were fixed. The results of the refinements are summarized in Tables I and II. Figure 1 shows a pictorial representation of the crystal structure of La_2CuO_4 . Here it can be seen that the thermal atomic vibrations of both the O1 and O2 atoms are enhanced as a consequence of soft octahedral tilting modes known from prior work.²⁰ The thermal parameters do not change significantly in the refinements using the lower-symmetric monoclinic space groups described below.

In order to check for a possible lower symmetry of the crystal structure, we measured reflections that are forbidden in $Bmab$. Multiple scattering could be excluded by the use of psi scans. Further, the intensities of these reflections have been measured at the different neutron wavelengths 0.884 \AA and 2.39 \AA . For all samples, we found systematically additional, very low intensities (about three orders of magnitude smaller than the strongest reflections) on $0k0$ with $k=\text{odd}$, $hk0$ with $h=\text{even}$, $k=\text{odd}$ and $h0l$ with $h, l=\text{odd}$. These conditions imply the absence of the glide planes a and b . This means that the translation of the atoms along the a and b axes is no longer necessarily $t=a/2$ and $t=b/2$. Due to the lower symmetry, one can expect an additional distortion of the CuO_6 octahedra. On the other hand the reflections are limited by the condition $h+l=2n$. Those reflections $h0l$, either with $h=\text{even}$ and $l=\text{odd}$ or with $h=\text{odd}$ and $l=\text{even}$, were found to be systematically absent. This implies the presence of a B -centered lattice. The highest-symmetry space group compatible with these constraints is the monoclinic space group $B2/m$ ($B 2/m 1 1$). In this structure, the octahedral distortions in all CuO_2 planes are identical due to the translation $t=(a+c)/2$.

Our structure refinements in the space group $B2/m$ showed that the intensities of the 45 reflections $0k0$ ($k=\text{odd}$) and $hk0$ ($h=\text{even}$) were calculated much smaller than the corresponding observations. Therefore we carried out refinements in the lower-symmetric noncentrosymmetric space

TABLE I. Positional and thermal parameters of La_2CuO_4 at 325 K as obtained from the structure refinement in the orthorhombic and monoclinic space groups $Bmab$ and $Bm11$, respectively. For the refinement in $Bm11$ several parameters were constrained to be equal. In these cases the standard deviation is listed only for one of the equal parameters.

La ₂ CuO ₄ : $a=5.3568(6)$ Å, $b=5.4058(5)$ Å, $c=13.1432(11)$ Å.											
Atom	<i>Bmab</i>	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	<i>occ</i>
La	8 <i>f</i>	0	-0.00672(4)	0.36145(2)	0.71(2)	0.62(1)	0.44(1)	0	0	-0.04(1)	1.0001(10)
Cu	4 <i>a</i>	0	0	0	0.33(2)	0.28(1)	0.88(2)	0	0	0.02(1)	0.9991(15)
O1	8 <i>e</i>	$\frac{1}{4}$	$\frac{1}{4}$	-0.00719(3)	0.68(2)	0.55(1)	1.43(2)	-0.19(2)	0	0	1.0016(14)
O2	8 <i>f</i>	0	0.03406(10)	0.18367(3)	2.08(3)	1.57(2)	0.66(2)	0	0	0.09(1)	0.9925(16)
Atom	<i>Bm11</i>	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	<i>occ</i>
La1	2 <i>a</i>	0	-0.00669(6)	0.36149(2)	0.70(2)	0.62(1)	0.43(1)	0	0	-0.02(1)	0.993(3)
La2	2 <i>a</i>	0	0.00669	0.63851	0.70	0.62	0.43	0	0	-0.02	0.993
La3	2 <i>a</i>	0	0.50669	0.86149	0.70	0.62	0.43	0	0	-0.02	0.993
La4	2 <i>a</i>	0	0.49331	0.13851	0.70	0.62	0.43	0	0	-0.02	0.993
Cu1	4 <i>a</i>	0	0.0010(6)	-0.00156(6)	0.36(2)	0.35(2)	0.93(2)	0	0	-0.02(1)	1.023(4)
Cu2	4 <i>a</i>	$\frac{1}{2}$	0.4997(5)	0.00156	0.36	0.35	0.93	0	0	-0.02	1.023
O11	4 <i>a</i>	$\frac{1}{4}$	0.2497(7)	-0.00705(4)	0.70(2)	0.56(2)	1.46(2)	-0.03(9)	-0.05(2)	-0.01(1)	1.000(4)
O12	4 <i>a</i>	$\frac{1}{4}$	0.7496(7)	0.00705	0.70	0.56	1.46	-0.03	-0.05	-0.01	1.000
O21	2 <i>a</i>	0	0.0300(4)	0.18365(3)	2.03(3)	1.50(2)	0.67(2)	0	0	-0.00(2)	0.991(4)
O22	2 <i>a</i>	0	-0.0380(4)	-0.18365	2.03	1.50	0.67	0	0	-0.00	0.991
O23	2 <i>a</i>	$\frac{1}{2}$	0.5380(4)	-0.18365	2.03	1.50	0.67	0	0	-0.00	0.991
O24	2 <i>a</i>	$\frac{1}{2}$	0.5300(4)	0.18365	2.03	1.50	0.67	0	0	-0.00	0.991

The thermal parameters U_{ij} (given in 100 \AA^2) are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{13}hla^*c^*)]$.

groups $B2$ ($B 2 1 1$) and Bm ($B m 1 1$). The better fit resulted from a refinement in Bm with $R_F=0.027$, $wR_F=0.030$, and $g.o.f=4.63$. In comparison the refinement in $B2$ resulted in the values $R_F=0.030$, $wR_F=0.032$, and $g.o.f=5.06$. Here it has to be mentioned that some of the refineable parameters were highly correlated, with correlation coefficients exceeding 90%. {The correlation coefficient between two parameters p_i and p_j is obtained from the covariance, i.e., the second moment with respect to p_i and p_j by normalization $\text{corr}(p_i, p_j) = \text{cov}(p_i, p_j) / [\sigma(p_i)\sigma(p_j)]$, where σ denotes the standard deviation.} Therefore we used constraints restricting the values of particular positional parameters. This has been done for the positional parameters of the lanthanum atoms, since they should not be influenced by additional distortions of the CuO_6 octahedra. Further constraints of the z param-

TABLE II. Interatomic distances (Å) and angles (°) of La_2CuO_4 at 325 K as obtained from the structure refinement in the orthorhombic $Bmab$.

La ₂ CuO ₄	
Cu–O1	1.9049(1)
Cu–O2	2.4210(5)
O1–Cu–O1	90.66(1)/89.34(1)
La–O1	2.5885(4)
La–O2	2.3470(5)
La–O2	2.5523(7)

eters were applied for the other atoms. Attempts of systematic refinements showed that the loss of the translational component of $t=b/2$ for the apical oxygen atoms (in Bm :

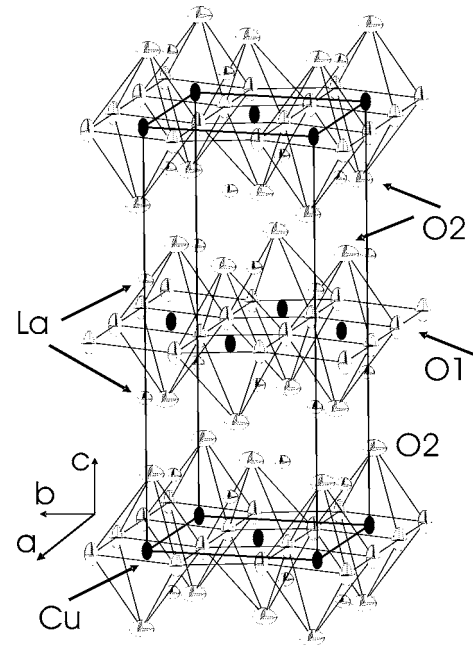


FIG. 1. Crystal structure of La_2CuO_4 at 325 K. Shown are the distorted corner-shared CuO_6 octahedra in the ab plane. The thermal ellipsoids of the atoms are plotted at the 90% probability level.

TABLE III. Observed and calculated structure factors obtained from the structure refinements in the monoclinic space group Bm ($Bm11$). In the table only the structure factors are listed that are systematically zero in $Bmab$.

$h k l$	F_{obs}^2	F_{cal}^2	$h k l$	F_{obs}^2	F_{cal}^2	$h k l$	F_{obs}^2	F_{cal}^2
2 1 0	0.25	0.11	3 0 1	0.29	0.03	1 0 9	0.21	0.24
4 1 0	0.21	0.09	5 0 1	0.28	0.02	3 0 9	0.35	0.27
6 1 0	0.09	0.07	7 0 1	0.20	0.03	5 0 9	0.23	0.20
0 3 0	0.30	0.25	1 0 3	0.28	0.09	1 0 11	0.22	0.28
2 3 0	0.21	0.24	3 0 3	0.31	0.10	3 0 11	0.22	0.32
4 3 0	0.25	0.20	5 0 3	0.20	0.07	5 0 11	0.22	0.23
6 3 0	0.17	0.15	7 0 3	0.21	0.10	1 0 13	0.25	0.32
0 5 0	0.24	0.20	1 0 5	0.32	0.14	3 0 13	0.26	0.36
2 5 0	0.18	0.19	3 0 5	0.28	0.16	5 0 13	0.28	0.27
4 5 0	0.20	0.16	5 0 5	0.18	0.11	1 0 15	0.31	0.35
6 5 0	0.16	0.16	7 0 5	0.25	0.17	3 0 15	0.34	0.39
0 7 0	0.02	0.02	1 0 7	0.37	0.19	5 0 15	0.26	0.30
2 7 0	0.02	0.02	3 0 7	0.30	0.22	1 0 17	0.29	0.38
4 7 0	0.02	0.01	5 0 7	0.25	0.16	1 0 19	0.29	0.39
1 0 1	0.34	0.03	7 0 7	0.24	0.23	1 0 21	0.28	0.40

four atoms, each in the Wyckoff position $2a$) has the strongest influence on the intensities of the reflections forbidden in $Bmab$. As obtained from our refinements, the apical oxygen atoms O21 (in $0, y, z$) and O22 (in $0, -y, -z$) show a shift $\Delta y = -0.022(2)$ Å; the apical oxygen atoms O23 (in $0, \frac{1}{2} + y, z$) and O24 (in $0, \frac{1}{2} - y, -z$) of the neighboring octahedra along b show a shift with the same value Δy in the opposite direction. On the other hand, shifts of the copper atoms two atoms, each in $2a$) and the in-plane oxygen atoms (two atoms, each in $4b$) seem to be weak. The results of the refinement are summarized in Table I. In Table III it can be seen that the agreement between the observed and calculated structure factors is reasonable, albeit not fully satisfactory. A more precise determination of the atomic positions is prevented by high correlations between the parameters, as discussed above.

In order to investigate the monoclinic distortion of the Bravais lattice, we have further collected high-resolution synchrotron powder diffraction data of La_2CuO_4 at 100 K. The presence of a monoclinic lattice should be clearly manifested by a splitting of particular reflections. Rietveld refinements were carried out in the monoclinic space group $B2/m$. Our refinements finally did not show any evidence of a monoclinic distortion, but from our data analysis we were able to place upper bounds of 0.02° on possible deviations of α , β , and γ from 90° .

Structure refinements were also carried out on the doped compounds $\text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4$ and $\text{La}_{1.97}\text{Sr}_{0.03}\text{CuO}_4$ from data sets collected at room temperature with a total of 1359 (472 unique) and 1056 (460 unique) reflections, respectively. The refined atomic parameters within $Bmab$ were in a good agreement with those obtained for the pure compound given in Table I. Additional reflections indicating monoclinic distortions of magnitude comparable to that of La_2CuO_4 were also detected in both compounds. Therefore we can conclude that the deviation from the previously reported orthorhombic

symmetry, i.e., a monoclinic distortion with the space group Bm , is intrinsic for pure and lightly doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

B. Magnetic structure

In view of the complex crystal structure discussed above and the magnetic field induced spin reorientations to be discussed below, we begin this section with a brief review of possible magnetic structures in the framework of Bertaut's representation analysis.^{21,22} Within the space group $Bmab$ the copper atoms are located at the Wyckoff position $4a$ in the point symmetry $2/m\cdots$ with the four positions $0,0,0$ (1), $0, \frac{1}{2}, \frac{1}{2}$ (2), $\frac{1}{2}, 0, \frac{1}{2}$ (3), and $\frac{1}{2}, \frac{1}{2}, 0$ (4). The basis functions of the spin sequences at these positions are denoted as follows: $F(++++)$, $G(+--+)$, $C(++--)$, and $A(++-+)$. Table IV lists the compatibility relations between these modes resulting from the representation analysis.

TABLE IV. Representations of the base vectors of $\{\text{Cu}\}$ in La_2CuO_4 with the space group $Bmab$. The copper atoms are located at the Wyckoff position $4a$: $0,0,0$ (1), $0, \frac{1}{2}, \frac{1}{2}$ (2), $\frac{1}{2}, 0, \frac{1}{2}$ (3), and $\frac{1}{2}, \frac{1}{2}, 0$ (4). The modes are $F(++++)$, $G(+--+)$, $C(++--)$, and $A(++-+)$.

$Bmab$	x	y	z
Γ_1	G_x	\cdots	\cdots
Γ_2	\cdots	G_y	F_z
Γ_3	F_x	\cdots	\cdots
Γ_4	\cdots	F_y	G_z
Γ_5	C_x	\cdots	\cdots
Γ_6	\cdots	C_y	A_z
Γ_7	A_x	\cdots	\cdots
Γ_8	\cdots	A_y	C_z

TABLE V. Representations of the base vectors of {Cu} in La_2CuO_4 with the space group $B2/m$. The copper atoms are located at the Wyckoff position $2a$ [in $0,0,0$ and $\frac{1}{2},0,\frac{1}{2}$] and $2d$ [in $\frac{1}{2},\frac{1}{2},0$ and $0,\frac{1}{2},\frac{1}{2}$]. The modes are $F(++)$ and $A(+)$.

$B2/m$	x	y	z
Γ_1	F_x	\dots	\dots
Γ_2	A_x	\dots	\dots
Γ_3	\dots	A_y	A_z
Γ_4	\dots	F_y	F_z

For completeness, we also show the results of the representation analysis in the monoclinic space group $B2/m$ in Table V. Here one finds two different copper atoms at the Wyckoff position $2a$ (in $0,0,0$; $\frac{1}{2},0,\frac{1}{2}$) and $2d$ [in $\frac{1}{2},\frac{1}{2},0$; $0,\frac{1}{2},\frac{1}{2}$]. The two magnetic moments of each site can couple either ferromagnetically or antiferromagnetically as designated with the notations $A(+)$ and $F(++)$. The two copper sublattices are decoupled, and their type of magnetic order must not necessarily be the same. However, the results presented in Sec. III A indicate that the monoclinic distortion is very weak, so that its effect on the magnetic structure is almost certainly negligible. Therefore, we present our data in the framework of the space group $Bmab$.

For La_2CuO_4 the strongest magnetic intensity was observed at the position of the reflection 100, in agreement with prior work.^{2,23} In Fig. 2 it can be seen that the intensity of the reflection 100 vanishes at the Néel temperature $T_N = 316(2)$ K. This is in good agreement with the values $T_N = 325$ K and $T_N = 310$ K of fully oxygenated samples reported earlier.^{2,11} This suggests that the magnetic moments of the copper atoms are ferromagnetically aligned in the bc plane and with antiferromagnetic coupling along the x direction. Our refinements showed that the magnetic moments are aligned parallel to the b axis. This is also in agreement with the magnetic structure presented earlier.^{2,23,24} In the notation introduced above, the primary magnetic mode is thus C_y .

Reflections corresponding to G or A modes were not detected. If C_x or C_z modes (which are allowed in $B2/m$) were present, magnetic intensity should appear on the position of

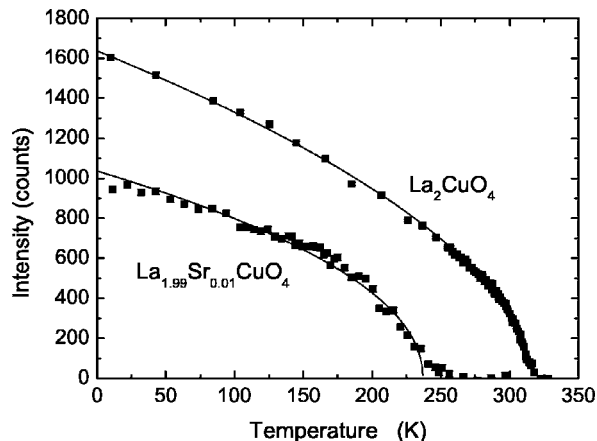


FIG. 2. Temperature dependence of the intensity of the 100 magnetic Bragg reflections of La_2CuO_4 and $\text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4$.

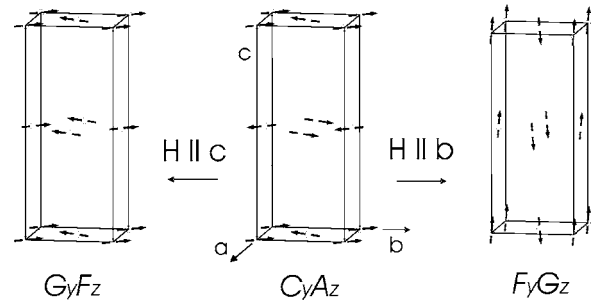


FIG. 3. Magnetic structure types of La_2CuO_4 . Shown are the magnetic structure in zero field (middle) and applied magnetic field parallel to the b and c axes. The components with the modes $F_z(H//c)$, $A_z(H=0)$, and $F_y(H//b)$ are rather weak. For clarity, they are exaggerated in the figures.

the reflection 010. We have seen above that weak intensity of structural origin is present at this position. At lower temperature, the intensity at 010 increases slightly. If the difference between the structure factors at 10 K and 325 K is attributed to magnetic ordering, it would correspond to a small moment of $0.060 \mu_B$ along the a axis. However, the more likely origin of the difference in 010 is not a magnetic but a nuclear effect, i.e., a slight increase of the monoclinic distortion with decreasing temperature. This confirms that the magnetic coupling along the x direction is antiferromagnetic, which results in a C_y magnetic structure. It can be seen in Table IV that the mode C_y is compatible with the mode A_z . This mode was not detected directly in our neutron diffraction experiments, but a weak A_z contribution has been inferred from an analysis of the uniform susceptibility.²⁵ The full magnetic structure including both modes is shown in Fig. 3. From the refinement of five strong magnetic reflections at 10 K, we obtained a sublattice magnetization of $0.42(1) \mu_B$, resulting in a residual $R_F(\text{mag}) = 0.027$. We note that this value was derived based on the isotropic Cu form factor of Ref. 18. However, the value will not be modified substantially if the anisotropic form factor of the Cu $d_{x^2-y^2}$ orbital is used.²⁶

Our $\text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4$ crystal exhibits a smaller Néel temperature of $227(2)$ K (Fig. 2), but the magnetic structure of the doped cuprate is identical to that of La_2CuO_4 . The saturated sublattice magnetization of $0.35(2) \mu_B$ is also smaller than that of pure compound. For $\text{La}_{1.97}\text{Sr}_{0.03}\text{CuO}_4$, no magnetic reflections were detected, consistent with the magnetic phase diagram reported earlier.^{1,6}

C. Magnetic field-dependent measurements

We now turn to the magnetic field-dependent experiments, beginning with fields applied parallel to the copper-oxide planes. During these measurements we noticed that twin domains had reappeared in the La_2CuO_4 crystal, probably due to the experimental treatment (i.e., repeated heating and cooling), which might result in strains induced *in situ* by magnetostriction. It was hence not possible to fully discriminate between situations in which the field is applied along the two in-plane directions a and b . The intensities of the magnetic reflections 100 and 102 were observed to decrease

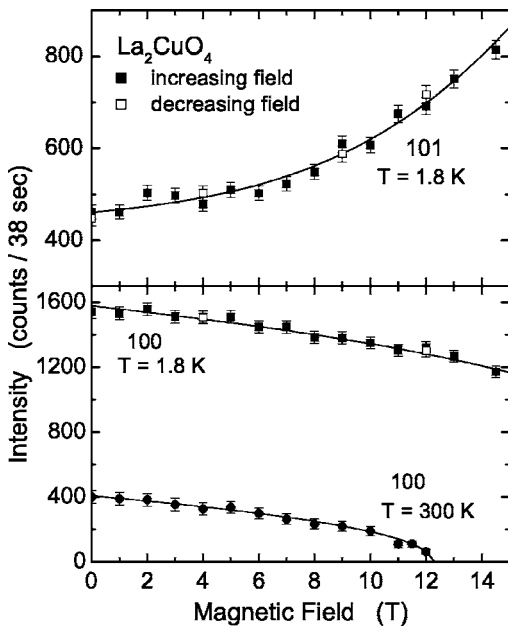


FIG. 4. Magnetic field dependence of the magnetic Bragg reflections 100 and 101 of La_2CuO_4 for a magnetic field applied within the ab plane.

continuously in an in-plane field, while those of the reflections 101 and 103 increased. In Fig. 4 it can be seen that this effect is fully reversible, and no hysteresis effects were observed. At 1.8 K, the 100 intensity decreases by about 20% in an applied field of 14.5 T (Fig. 4). An extrapolation based on a power law behavior (see lines in Fig. 4) yields a critical magnetic field of about 22 T. For higher temperatures, the critical field is reduced and reaches a value of 12.3 T at a temperature of 300 K. This is close to the Néel temperature of 316(2) K (Fig. 2). These critical fields are comparable to, albeit somewhat higher than, those reported in magnetoresistance experiments on $\text{La}_{1.99}\text{Sr}_{0.01}\text{CuO}_4$.¹⁰

The field dependence of the magnetic intensities clearly suggests that the C -type ordering is continuously reduced with increasing field, and that a G -type ordering is induced. The moment direction of the induced order can be determined from the intensity ratio $I(101)/I(103)$. We found a ratio of about 3, which is consistent with a moment direction parallel to the c axis. In contrast, models with moments parallel to a and b yield ratios of about 0.3 and 1, respectively, inconsistent with the data. The field-induced G_z order we have found is in full agreement with the one inferred from Raman scattering work in magnetic fields along the b axis.^{11,12} The results of the representation analysis given in Table IV show that the G_z mode is compatible with the ferromagnetic mode F_y , which is too weak to be detectable directly in our neutron diffraction study. The estimated upper bound is $5 \times 10^{-3} \mu_B$, which is compatible with values inferred from magnetization measurements.¹⁴ The lowering of the Zeeman energy along b allowed by this mode explains the origin of the field-induced spin reorientation and further supports the conclusions of Refs. 11 and 12. The full magnetic structure in a large b -axis oriented field is shown in Fig. 3.

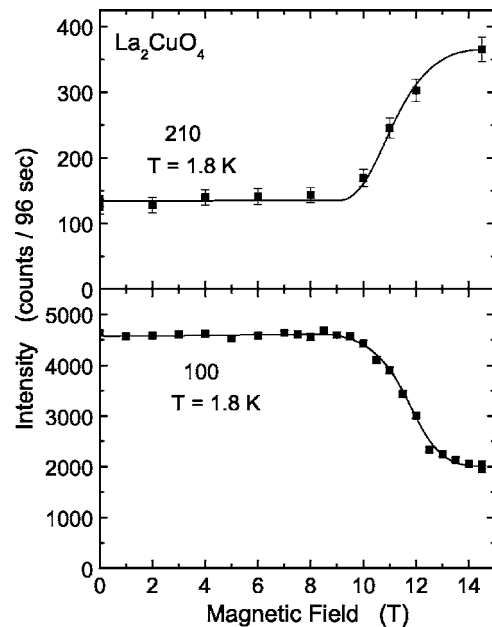


FIG. 5. Magnetic field dependence of the magnetic reflections 100 and 210 of La_2CuO_4 for a magnetic field applied parallel to the c axis, measured at $T=1.8$ K. The data were taken with increasing field. Lines are guides to the eye.

The positions, intensities, and linewidths of nuclear Bragg peaks of the form $h0l$ and $0kl$ with $h, k, l = \text{even}$ (allowed in the orthorhombic space group $Bmab$) did not show any field dependence up to 12 T. Unfortunately our cryomagnet did not allow us to reach magnetic fields exceeding 12 T at a sample temperature of 300 K. Therefore we were not able to probe whether the field-driven spin reorientation transition is related to the magnetic field induced detwinning of La_2CuO_4 observed by Lavrov *et al.* in a magnetic field of 14 T at room temperature.⁹

Figure 5 shows the dependence of the intensities of the magnetic Bragg reflections 100 and 210 on a magnetic field applied parallel to the c axis. At a field of $H_c = 11.5$ T the 100 intensity decreases, whereas the 210 intensity increases. In contrast to the measurements in an in-plane field, an abrupt change of the intensity was observed, and this phase transition shows a hysteresis with a field width of about 1.5 T. This behavior results from a field-induced $G_y F_z$ mode, as reported by Kastner *et al.* at a critical field of 4.8 T in a nonstoichiometric sample with a correspondingly reduced Néel temperature of 234 K.²⁷ A ferromagnetic moment of $\mu_z \sim 10^{-3} \mu_B$ was determined from magnetic measurements.^{14,25} This moment (as well as the corresponding A_z component at zero field) is too small to be detectable by neutron scattering. The high-field magnetic structure is depicted in Fig. 3. The origin of this transition was discussed at length in prior work.^{14,25} Here we note briefly that the high-field spin structure is compatible with the representation analysis of Table IV, and that the critical field is lower than that of the transition induced by the in-plane magnetic field, because the Zeeman energy competes against the exchange anisotropy as well as the interplanar exchange coupling. An aspect to be resolved by future work is the deviation of the

transition field from that observed by Raman spectroscopy on samples synthesized in a similar way.¹¹ This could reflect different heat treatment of the samples and/or measurement temperatures of the samples.

IV. CONCLUSIONS

In summary, our determination of the magnetic structure in high-magnetic fields confirms the magnetic field-induced spin reorientations indicated by prior work on pure and lightly doped La_2CuO_4 , which had yielded indirect information in this regard. These reorientations are driven by the interplay between the Zeeman energy, the weak exchange coupling between the CuO_2 layers, and the exchange anisotropies. The phenomena discussed here may also be of interest for models of magnetic correlations in superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, because both the zero-field²⁸ and the magnetic-field-induced²⁹ incommensurate magnetic order recently observed in doped La_2CuO_4 exhibit at least short-

range interplanar correlations as well as residual exchange anisotropies. We also discovered a subtle monoclinic distortion of the crystal structure of pure and lightly Sr-doped La_2CuO_4 , which results predominantly from displacements of the apical oxygen atoms. These displacements are small, but as the pinning of charge stripes in doped La_2CuO_4 appears to be determined by subtle crystallographic details,³ they may well be relevant for a complete understanding of the charge transport in this system as well.

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