Magnetoelectric effect and phase transitions in CuO in external magnetic fields

Zhaosheng Wang1, Navid Qureshi2, Shadi Yasin1,3, Alexander Mukhin4, Eric Ressouche5, Sergei Zherlitsyn1, Yurii Skourski1, Julian Geshev6,7, Vsevolod Ivanov4, Marin Gospodinov8 & Vassil Skumryev7,9

Apart from being so far the only known binary multiferroic compound, CuO has a much higher transition temperature into the multiferroic state, 230 K, than any other known material in which the electric polarization is induced by spontaneous magnetic order, typically lower than 100 K. Although the magnetically induced ferroelectricity of CuO is firmly established, no magnetoelectric effect has been observed so far as direct crosstalk between bulk magnetization and electric polarization counterparts. Here we demonstrate that high magnetic fields of $\approx 50 \text{T}$ are able to suppress the helical modulation of the spins in the multiferroic phase and dramatically affect the electric polarization. Furthermore, just below the spontaneous transition from commensurate (paraelectric) to incommensurate (ferroelectric) structures at 213 K, even modest magnetic fields induce a transition into the incommensurate structure and then suppress it at higher field. Thus, remarkable hidden magnetoelectric features are uncovered, establishing CuO as prototype multiferroic with abundance of competitive magnetic interactions.

1 Hochfeld-Magnetlabor Dresden (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, D-01314 Dresden, Germany. 2 Institut Laue Langevin, 6 rue Jules Horowitz, Bât. Postale 156, F-38042 Grenoble, France. 3 American University of the Middle East, College of Engineering and Technology, 54200 Egaila, Kuwait. 4 Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, Moscow 119991, Russia. 5 SPSM, UMR-E CEA/UJF-Grenoble 1, INAC, F-38054 Grenoble, France. 6 Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, 91501-970 Rio Grande do Sul, Brazil. 7 Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain. 8 Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria. 9 Institut Català de Recerca i Estudis Avançats, E-08010 Barcelona, Spain. Correspondence and requests for materials should be addressed to S.Z. (email: s.zherlitsyn@hzdr.de) or to Y.S. (email: i.scurschii@hzdr.de) or to V.S. (email: vassil.skumryev@uab.es).
A s a building block of high-temperature superconductors, CuO (tenorite) has been extensively studied following their discovery. Unlike other 3d-metal monoxides, CuO has a monoclinic crystal structure described by the centrosymmetric space group C2/c. Magnetic order sets in at the Neél temperature \( T_{N_2} \approx 230 \text{ K} \) and the magnetic moments order-2 to incommensurate helix with an envelope oblique to the propagation vector \( q \) (oblique helix), the so-called AF2 phase. Another transition to a collinear commensurate antiferromagnetic structure, AF1, with the moments along the monoclinic \( b \) axis, takes place at \( T_{N_1} \approx 213 \text{ K} \).

Several findings, namely multiferroicity of the AF2 phase, electromagnons and presence of toroidal moments, have triggered renewed interest in CuO. Furthermore, it was recently suggested that room-temperature multiferroicity (which is expected to take place at \( T_{N_1} \)) could be explained equally well by a collinear model with the moments along the \( b \) axis. This is consistent with the high-field data within the incommensurate phase, suggesting that a third phase, AF3, with presumably long-pitched magnetic structure is often evidenced by magnetic-demonstrated that an electric field could partly change the polarization, and ultrasound velocity at relatively low magnetic fields. The results of our magnetic susceptibility, magnetic torque, magnetocapacitance, thermal expansion, ultrasound velocity and single-crystal neutron diffraction experiments (Supplementary Notes 1 and 2 and Supplementary Figs 1,2 and 3) are in general agreement with the known sequence of the temperature-induced magnetic transitions at zero magnetic field, that is, successive AF1 \( \rightarrow \) AF2 \( \rightarrow \) paramagnetic state transitions. The refined magnetic structures are visualized in Fig. 1a,b,d.

Results
Zero magnetic-field magnetic structures and transitions. The results of our magnetic susceptibility, magnetic torque, magnetocapacitance, thermal expansion, ultrasound velocity and single-crystal neutron diffraction experiments (Supplementary Notes 1 and 2 and Supplementary Figs 1,2 and 3) are in a general agreement with the known sequence of the temperature-induced magnetic transitions at zero magnetic field, that is, successive AF1 \( \rightarrow \) AF2 \( \rightarrow \) paramagnetic state transitions. The refined magnetic structures are visualized in Fig. 1a,b,d.

Magnetic-field-induced transitions. Magnetic-field-induced transition into a high-field (HF1) phase takes place when the magnetic field \( H \) is applied along the \( b \) axis within the collinear AF1 phase below 213 K (ref 19.29). The transition is believed to be of a spin– flop type with the magnetic moments fopping perpendicular to \( H \), thus causing a jump of the magnetization at the critical field \( H_{c1} \). As seen in the magnetization curves (Fig. 2a), \( H_{c1} \approx 10.5 \text{ T} \) at 2 K. The field-induced transition is reflected in some of the neutron diffraction reflections (Supplementary Fig. 3b). We have refined the magnetic structure, unknown before, of this HF1 phase at 12 T. It consists of collinearly aligned moments \([0.51(1)\mu_B] \) within the \( ac \) plane at an angle of \( 26(2)^\circ \) from the \( c \) axis towards the positive \( a \) axis (Fig. 1c). Note that, importantly, this direction is close to the second axis of the helical envelope, that is, the collinear magnetic moments flop from one envelope axis to the other, perpendicular to \( H \).

As expected, \( H_{c1} \) increases with \( T \rightarrow T_{N_1} \approx 213 \text{ K} \), that is, towards the commensurate–incommensurate transition temperature at \( H = 0 \) (Fig. 2a). Surprisingly, we found that \( H_{c1} \) suddenly decreases at the vicinity of \( T_{N_1} \), as shown in the magnetization curve at 212 K. The magnetic-field evolution of the neutron diffraction rocking curves at 212 K (Fig. 2c) reveals a transition from the nonpolar collinear AF1 to an incommensurate magnetic structure with \( q = (0.509 \pm 0.000 \pm 0.483) \) as in the polar AF2 phase, with the two magnetic phases coexisting in a range of fields around 10.5T as implied by the overlap of the respective intensities. This observation strongly suggests that an electric polarization could eventually appear under application of modest magnetic fields at temperatures just below \( T_{N_1} \), which would constitute evidence for a magnetoelectric effect. To verify this suggestion, integrated magnetic-peak intensities were collected below 211.4 K. The zero-field diffraction data can be explained by the collinear low-temperature model, that is, the magnetic moments \([0.29(1)\mu_B] \) at this temperature are collinearly aligned along the \( b \) axis. At this temperature, a magnetic field of 12 T is just enough to induce a transition into the incommensurate oblique helical phase with \( q = (0.509 \pm 0.000 \pm 0.483) \) (first envelope axis: \( 0.22(2)\mu_B \) along the \( b \) axis; second envelope axis: \( 0.34(4)\mu_B \) at an angle of \( 20(6)^\circ \) from the \( c \) axis), that is, into the AF2 phase. We note that the high-field data within the incommensurate phase could be explained equally well by a collinear model with the moments within the \( ac \) plane (as the HF1 structure). However, the symmetry of this magnetic model is not compatible with the observed macroscopic electric polarization described below.

The limited neutron diffraction data set, due to the aperture of the cryomagnet, namely lacking magnetic Bragg reflections with non-zero \( k \)-indices, is the reason why we cannot unambiguously determine the complex magnetic structure by the performed...
In search for a field-induced transition within the multiferroic system investigated by single-crystal neutron diffraction alone. It is worth noting that the ultrasound velocity measurements (Fig. 2b and also Supplementary Note 3 and Supplementary Fig. 4) reveal that the magnetic-field-induced transition for $T < 211.5$ K is actually reflected in two ultrasound anomalies, a result that we attribute to the fact that in a real sample the spin–flop occurs via an intermediate state existing within few kOe, as our magnetization curves show (Fig. 2a), and softening of the sound velocity at two fields of magnetic instability: for the low-field AF1 and for the high-field HF1 phases, correspondingly. In addition, note that this two-stage behaviour disappears for $T > 211.5$ K but lower that $T_{N1}$, which is consistent with AF1 to AF2 field-induced transition taking place in this temperature range.

In search for a field-induced transition within the multiferroic incommensurate AF2 phase (from 213 to 230 K, approximately), the magnetization at 218 K has been recorded in pulsed magnetic fields as high as 60 T applied along the $b$ axis, that is, along two perpendicular axes of the helical envelope. For those two directions, one would expect a sharp change of magnetization at a critical field for which the plane of the magnetic helix is reoriented in a direction close to orthogonal with respect to $H$. This would result in switching $P$ from $b$ to $a$ or $c$ axes. However, note that other high-field spin configurations including collinear structures cannot be ruled out. The latter scenario would lead to $P = 0$ in the high-field phase. The magnetization measured in both directions fails to provide unambiguous proof for any field-induced transitions. This, however, could be a consequence of the proximity of $T_N$ and the specific characteristics of the zero-field helical structure, both of them influencing the sharpness of the expected spin–flop transition. We also note (Supplementary Fig. 5) that the magnetization at 60 T is $\sim 0.07 \mu_B$ per formula unit, much smaller than that expected for a spin–flip ‘ferromagnetic’ alignment of spin $1/2$ Cu$^{2+}$ (forced by $H$) with a moment of $1\mu_B$, thus reflecting the strength of the exchange coupling interactions.

**Magnetic-field effect on electric polarization.** Next, we turn to the other counterpart, electric polarization, $P$, which is known to exist at zero magnetic field in the AF2 phase and is directed along the monoclinic $b$ axis. As a direct probe of polarization changes, the pyrocurrent was measured in pulsed magnetic field $H_b$ applied along the $b$ axis. Figure 3a shows that at $\sim 215.5$ K, a temperature that is well inside the AF2 phase, the pyrocurrent $I_P$ measured along $b$ reveals either a maximum or a minimum at $H \approx 37$ T, depending on the sign of the poling electric field $E$ ($\sim 170$ V mm$^{-1}$) in which the sample was cooled from $T > T_{N2} \approx 230$ K (or alternatively warmed up from $T < T_{N1} \approx 213$ K) to ensure a predominant orientation of the polar domains. Such a behaviour constitutes a clear fingerprint of a magnetoelectric effect within the incommensurate phase, implying in turn a field-induced magnetic transition and consequent polarization change. A tiny hump was recorded on $I_P$, indicating a field-induced magnetic transition and consequent polarization change. A tiny hump was recorded on $I_P$.
at $H \approx 37$ T, for the descending branches of the $H$-pulse. Note that no $E$ was present during the $H$-pulse in the above measurement. The tiny change of $I_b$ on reducing $H$ should be attributed to only small misbalance in the number of magnetic domains with opposite chirality when the AF2 phase is re-entered without $E$ applied (see also Supplementary Note 4). In fact, when an electric field equal to the poling $E$ holds during the $H$-pulse (Supplementary Fig. 6a), the changes of $I_b$ for the two branches of the magnetic field sweep are similar in magnitude (since the balance between the magnetic domain with left and right chirality is impaired on re-entering the AF2 phase under $E$) and opposite in sign. The small difference in the positions of the maximum and the minimum of $I_b$ could be attributed to a hysteresis in the field-induced transition (presumably of first-order type) and/or to dynamic effects\(^{30}\).

A special case among the $I_b(H_b)$ is the one measured at temperatures just below $T_{N1} \approx 213$ K, where no polarization should exist at $H = 0$, for example, at 212.5 K (Fig. 3b). Unlike $I_b(H_b)$ at temperatures between $T_{N1}$ and $T_{N2}$, where only one minimum and one maximum are observed for each of the ascending and descending branches of the $H$ sweep, at 212.5 K a maximum and minimum are seen for the ascending branch followed by a maximum and minimum for the descending branch. We recall that at 212 K we observed a field-induced AF1 $\to$ AF2 transition at $H_{c2} \approx 10$ T (Fig. 2). This critical field is in a good agreement with the lower field-induced transition manifested on the $I_b(H_b)$ data. Thus, we conclude that the two transitions manifested on each of the $I_b(H_b)$ branches are related to consecutive crossings of the borders between AF1 $\to$ AF2 $\to$ HF1 with $P_b = 0$ phase on increasing $H$ (and in reversed order, on decreasing $H$). This finding constitutes a solid proof for the magnetoelectric effect in CuO and particularly for the remarkable magnetic-field-induced appearance and disappearance of $P$ at a fixed temperature within a narrow temperature region below $T_{N1} \approx 213$ K.

The electric polarization estimated by integrating the pyrocurrent data with respect to time is plotted in Fig. 3 at some selected temperatures; the complete data set is given in Supplementary Fig. 6a. Because of the high coercivity of $P$, rather high poling fields are needed to establish a single-domain state\(^{18,31}\), which should be the reason for the slight underestimation of $P$ as compared with the highest literature values.

Ultrasound velocity and magnetostriction. To further probe the magnetic-field-induced transitions, we used magnetostriction and ultrasound techniques, both sensitive to spin–lattice coupling (Fig. 4).

The temperature dependence of the sound velocity change $\Delta v/v$ of the transverse ultrasonic wave propagating along $b$ \((k||b)\) and $u||c$ \((k||c)\) measured for $H$ \((0.000, 0.509)\) (Fig. 4a) reveals anomalies matching the known spontaneous transitions and those induced by $H$ as discussed above (see also Fig. 2b). The temperature hysteresis on the data below 213 K (the left bottom inset) reflects the first-order nature of the AF1 $\to$ AF2 transition in presence and in absence of $H$. Importantly, the ultrasound velocity data provide strong support to the recently promoted claim\(^{19-21,23}\) that an additional AF3 magnetic phase exists, sandwiched between the paramagnetic and the AF2 phases (top right inset) as well as for the evolution of its phase borders in presence of magnetic field. Because of the very narrow temperature interval of existence (just $\approx 0.2$ K at $H = 0$) and mainly because of its proximity to the paramagnetic state, our attempts to characterize this phase by neutron diffraction did not succeed. It is plausible to assume, by analogy with other monoclinic multiferroics (for example, MnWO$_4$), that the AF3 phase has an incommensurate sinusoidal collinear structure with a spin direction along $b$.

![Figure 2](image.png)

Figure 2 | Magnetic-field-induced transitions in CuO. (a) Magnetization curves at different temperatures. For temperatures below the transition into the AF1 phase at $T_{N1} = 213$ K, jumps of magnetization are observed at $H_{c1}$ for the magnetic-field-induced transitions; note the reduction in $H_{c1}$ for the 212 K data (see also the inset). (b) Magnetic-field dependence of the sound velocity $\Delta v/v$ of the transverse ultrasonic wave with wave vector $k$ propagating along the $b$ axis with polarization $u$ directed along $c$ axis \((k||b)\) and $u||c$ \((k||c)\) measured at different temperatures. Results for up and down field sweeps are shown. The data at different temperatures are shifted arbitrarily along the vertical axis for clarity. (c) Commensurate to incommensurate field-induced phase transition in CuO at 212 K: neutron rocking curves (rotation of the crystal around the diffractometer vertical axis) as a function of $H$. The position A3 = 162.8° corresponds to $q = (0.509 0.000 0.483)$, whereas A3 = 164.5° corresponds to $q = (0.509 0.000 -0.483)$. The scattered intensity is colour-coded between 0 and $2.86 \times 10^3$ counts per 6 s.

The magnetostriction at 212.4 K and for $H = 0$ (Fig. 4b) exhibits anomalies at the critical fields of $\approx 12$ and $\approx 17.5$ T in good agreement with the field-induced AF1 $\to$ AF2 and AF2 $\to$ HF1 transitions, respectively, as found in our magnetization and in the neutron diffraction experiments. Similarly, the critical field of $\approx 34$ T at 215.2 K corresponds to the transition from the AF2 to HF1 phase. We notice that the $b$ axis shrinks (since $\Delta L<0$) at the field-induced AF1 $\to$ AF2 transition taking place at $\approx 12$ T at 212.4 K. This agrees with the thermal expansion at the same spontaneous transition (Supplementary Fig. 7). At the
steady at low temperatures. However, more sensitive measurements in change takes place at this transition implying diminutive magnetostriction changes at the AF1 of the pulsed-field experiment, we were not able to detect transitions is rather similar. Within the experimental resolution We also note that the magnitude of the changes at those transitions is a result of small difference ($\sim 0.2$ K) between the temperatures for the two measurements. The arrows indicate increasing/decreasing $H$. (b) $I_p$ as a function of $H$ applied along the $b$ axis at two selected temperatures (slightly below 213 K and in the incommensurate phase above it). (c) $I_p$ as a function of $H$ applied along the distinct direction $a$ within the $ac$ plane. (d) The electric polarization $P_b$ along the $b$ axis at some selected temperatures, as a function of $H$ applied along the $b$ axis. (e) $P_b$ as a function of $H$ applied along the distinct direction $a$. The data recorded at increasing $H$ are presented by solid line, while the data at decreasing $H$ are presented by dashed line.

Figure 3 | Magnetic-field variation of the pyrocurrent and the electric polarization for the two axes of the helical envelope. (a) The pyrocurrent along the $b$ axis, $I_p$, as a function of the magnetic field $H$ applied along the $b$ axis, measured at $\approx 215.5$ K (within the incommensurate phase) after cooling through the Néel temperature in an electric field with different polarity ($\approx 170$ V mm$^{-1}$). The small shift between the two sets of data along the $T$ axis is a result of small difference ($\approx 0.2$ K) between the temperatures for the two measurements. The arrows indicate increasing/decreasing $H$. (b) $I_p$ as a function of $H$ applied along the $b$ axis at two selected temperatures (slightly below 213 K and in the incommensurate phase above it).

Figure 4 | Magnetostriction effect and magnetic-field effect on the sound velocity for $H$ along the $b$ axis. (a) Temperature dependence of the sound velocity $\Delta v/v$ of the transverse ultrasonic wave with wave vector $k$ propagating along the $b$ axis with polarization $u$ directed along $c$ axis ($|k||H|b$ and $u|c$) measured at different applied magnetic fields. Results for up and down temperature sweeps are shown. The (i) inset shows the sound velocity in the vicinity of the phase transitions $T_{N2}$ and $T_{N3}$ after subtracting the linear anharmonic contribution; the (ii) inset shows some details in the sound velocity at the phase transition $T_{HF1}$. The arrows indicate the anomalies at the phase transitions. The data at different $H$ are shifted arbitrary along the vertical axis for clarity. (b) Magnetostriction (the relative length change $\Delta L/L$) along the $b$ axis recorded in pulsed magnetic field along the same crystallographic axis at two selected temperatures.

same time, $b$ expands ($\Delta L > 0$) on the field-induced AF2 $\rightarrow$ HF1 transition at $\approx 17.5$ T for 212.4 K and at $\approx 34$ T for 215.2 K. We also note that the magnitude of the changes at those transitions is rather similar. Within the experimental resolution of the pulsed-field experiment, we were not able to detect magnetostriction changes at the AF1 $\rightarrow$ HF1 spin–flop transition at low temperatures. However, more sensitive measurements in steady $H$ show (Supplementary Fig. 8) that a minute positive $\Delta L$ change takes place at this transition implying diminutive $b$ axis expansion in the HF1 phase. At $T$ higher than $\approx 219$ K, no peculiarity has been detected within the resolution of any of our magnetostriction experiments. From the fact that $\Delta L$ is finite between the incommensurate AF2 and the two commensurate AF1 and HF1 phases but is much smaller between the two commensurate ones, we may draw the conclusion that the absence of measurable magnetostriction change at the transition into the high-temperature high-field phase favours an incommensurate phase. Considering the phase diagrams of
Figure 5 | The magnetoelectric phase diagrams of CuO. (a) Magnetic field $H$ versus temperature $T$ for $H||b$, based on pyrocurrent (blue dots), capacitance (green dots), magnetostriiction (pink dots), sound velocity (red dots) and bulk magnetization data (black dots). Dashed lines are expected hypothetical phase boundaries predicted from theoretical analysis. AF1 stands for collinear commensurate (CM) antiferromagnetic (AFM) structure, with the moments along the $a$ axis; HF1—collinear commensurate antiferromagnetic structure, with the moments perpendicular to the $b$ axis; AF2—hellicoidal, incommensurate (ICM) antiferromagnetic structure; AF3—incommensurate sinusoidal collinear structure with a spin direction along the $b$ axis; HF3—incommensurate sinusoidal collinear structure with a spin direction perpendicular to the $b$ axis. $P_b$ is the electric polarization along the $b$ axis.

(b) $H||a$ within the ac plane ($\approx 30^\circ$ from the c axis) based on pyrocurrent (blue dots) together with the hypothetical phase boundaries (dashed lines).

well-investigated multiferroics such as MnWO$_4$ or Ni$_3$V$_2$O$_8$, it is plausible to assume that this HF3 phase has a sinusoidal modulation with the moments perpendicular to $b$.

Magnetoelectric phase diagrams. Figure 5a displays the phase diagram for $H||b$ constructed on the base of the critical fields recorded on bulk magnetization, pyroelectric current, magnetostriiction, ultrasound and neutron diffraction data. Magnetocapacitance data (Supplementary Fig. 9) are also plotted. We note that only tiny changes in the pyrocurrent in the other two crystallographic directions, $I_a(H_a)$ and $I_b(H_b)$, were observed (probably because of spurious currents or/and such originating from the polar domain walls) implying that $P$ does not switch direction but vanishes on the $H$-driven transformation of AF2. Besides, we have sketched in the phase diagram the hypothetical$^{10}$ phase boundaries (dashed lines) between the sinusoidal collinear phases (along $b$ and perpendicular to it) and the paramagnetic phase.

The pyrocurrent $I_b$ was also measured for $H$ applied along the distinct direction $\alpha$ within the ac plane, which is the other axis of the helical envelope (Fig. 3b). Unlike $I_b(H_a)$, $I_b(H_b)$ is zero below $T_{N1} = 213$ K, while for $T$ between $T_{N1}$ and $T_{N2}$, $I_b$ has a similar trend and a single minimum/maximum for the ascending/descending branches of $H$, respectively. Again, only tiny changes in the pyrocurrent in the other two crystallographic directions, $I_a(H_a)$ and $I_b(H_b)$, were observed (probably because of spurious currents) implying that $P$ does not switch direction but vanishes on the $H$-driven transformation of AF2. The phase diagram constructed on the base of the critical fields recorded on the pyroelectric current together with the hypothetical phase boundaries is given in Fig. 5b.

Discussion

In what follows we will attempt to justify the constructed phase diagrams. According to the antiferromagnetic resonance data in the low-temperature collinear phase of CuO (refs 32,33), the resonance frequencies of two modes corresponding to spin oscillations closer to the $bc$ and $ba$ planes (strictly speaking, these planes should be the easy $xb$ and hard $xa$ planes where $\alpha = \alpha + 90^\circ$) are $\nu_1 = \gamma(2H_{A1}H_E + H_{A2}^2)^{1/2} \approx 308$ GHz and $\nu_2 = \gamma(2H_{A2}H_E + H_{A1}^2)^{1/2} \approx 1.852$ GHz, respectively, where $H_E$ is the exchange field and $H_{A1}$ and $H_{A2}$ are the anisotropy fields in the corresponding planes ($H_{A2} < H_E$). This implies that the $bc$ plane’s anisotropy energy exceeds that of the $bc$ plane by $\approx 36$ times since $\nu_2/\nu_1 = (2H_{A2}H_E + H_{A2}^2)/(2H_{A1}H_E + H_{A1}^2) \approx H_{A2}/H_{A1}$. It allows considering CuO as an ‘easy plane’ antiferromagnet, in which the helical phase can be stabilized only in the easy $bc$ plane. At zero magnetic fields, the development of the magnetic structure is governed by the fine balance between the exchange and the anisotropy energies. Just below the Neél temperature, the magnetic structure is determined by the exchange energy, favouring an incommensurate structure with spins along an easy $b$ axis, that is, a sinusoidal phase (AF3 promoted in refs 19–22, whose existence is supported by our work, see the top right inset in Fig. 4a). However, in this structure the gain in exchange energy is not full because of a strong reduction of the average local spins (magnetization) at some crystallographic sites owing to the collinear spin arrangement and the sinusoidal modulation of the moment size. To increase the gain in the exchange energy, the helical AF2 structure in an easy plane formed by the $xb$ spin rotation plane is developed in spite of some increase in the anisotropy energy. However, when the temperature is further lowered, this increase in the anisotropy energy becomes unfavourable and, to minimize the total energy, the system again goes to a collinear spin configuration along $b$ (AF1), although in a commensurate antiferromagnetic state (losing in exchange energy but gaining in anisotropy energy).

For $H||b$, one could expect a spin–flop of the cycloid to the ac plane. However, the strong anisotropy related with a spin declination towards the hard $a$ axis (more precisely, to the hard axis ‘$x$’ close to $a$) does not favour such an ac plane-flopped cycloid state. Instead, a field-induced transition into HF1 (as shown by our neutron data) or HF3 phases takes place (both having collinear structures with moments perpendicular to $b$). None of these two flopped magnetic structures supports polar order. Our data imply the existence of a triple point in the high-field part of the phase diagram at which the AF2–HF1, the AF2–HF3 and the HF1–HF3 phase boundaries meet, as well as the absence of the HF2 phase, that is, the supposedly flopped helix.

Similarly, for $H||a$ within the spin rotation plane one could expect an annihilation of the $a$ spin-component resulting in a commensurate or incommensurate sinusoidal modulation of magnetic moments along $b$.  


Thus, it seems that the role of the strong anisotropy of CuO discussed above has been underestimated in refs 19,20, where a detailed phase diagram has been simulated for $\mathbf{H} \parallel \mathbf{b}$. In the light of the above arguments, the predicted spin–flop helical phase HF2, which supports the polar order, should be absent and instead a direct transition between HF1 and HF3 phases should take place.

To conclude, magnetoelectric effect was observed in CuO—a prominent simple oxide with distinct position among the multiferroic materials, as suppression of the spontaneous electric polarization at high magnetic fields. Furthermore, it was found that just below the spontaneous magnetic transition from commensurate (paraelectric) to incommensurate (ferroelectric) phases, the relative length change $|\Delta L|$ reaches a remarkable value of 0.5 mm along the $b$ axis at room temperature, suggesting a nearly stoichiometric ratio of Cu and O.

**Methods**

**Crystal growth.** Single crystals of CuO were grown using the high-temperature solution growth method. The starting materials (minimum purity of 99.999%) were CuO powder and a flux of 95% $\text{Bi}_2\text{O}_3$ and 5% $\text{Bi}_2\text{O}_4$ in the ratio 20:1. The mixture was sealed in a platinum crucible, maintained at 1,150°C for 48 h and then slowly cooled to 920°C at a rate of 0.5 degrees per hour. At 920°C, the flux was removed from the crucible by decanting. The crystal quality was checked by neutron diffraction with a four-circle cryostat, as well as on the D23 diffractometer at ILL to have a reference point for the subsequent experiments with a magnetic field applied parallel to the crystallographic $b$ axis. Roughly, 500 unique magnetic reflections have been measured at selected temperatures within the commensurate phase and within the incommensurate phase. Symmetry analysis has been applied to deduce those magnetic moment configurations, which are compatible with the nuclear commensurate symmetry. The magnetic structures under an applied field along the $b$ axis have been analysed with a vertical cryomagnet at 235. Owing to the limited aperture of the cryomagnet, 50 unique magnetic reflections have been collected.

**Magnetization and torque measurements.** Magnetization and magnetic torque in d.c. fields up to 14 T were measured using commercial SQUID magnetometers from Quantum Design. None of the data have been corrected for ionic diamagnetic core contributions or for demagnetizing-field effect since those corrections are negligibly small. Pulsed-field magnetization was measured by integrating the voltage induced in a coil surrounding the sample. The system was precisely compensated before the pulse to cancel the $dB/dt$ contribution.

**Ultrasound measurements.** Ultrasound measurements in steady and pulsed magnetic fields were performed using a pulse echo technique. Two piezoelectric lithium niobate ($\text{LiNbO}_3$) resonance transducers were glued to opposite parallel surfaces to excite and detect acoustic waves. Transverse acoustic waves with wave frequency between 33 and 111 MHz.

**Pulsed magnetic fields.** The facilities at the Dresden High Magnetic Field Laboratory in Dresden were used. The experiments in this study were performed in pulsed magnetic fields up to 60 T with the pulse duration of 35 and 150 ms.

**Neutron diffraction.** The magnetic structures at zero magnetic field have been investigated on the D23 diffractometer (CEA CRG ILL, Grenoble) in combination with a four-circle cryostat, as well as on the D10 diffractometer at ILL. A reference point for the subsequent experiments with a magnetic field applied parallel to the crystallographic $b$ axis. Roughly, 500 unique magnetic reflections have been measured at selected temperatures within the commensurate phase and within the incommensurate phase. Symmetry analysis has been applied to deduce those magnetic moment configurations, which are compatible with the nuclear symmetry. The magnetic structures under an applied field along the $b$ axis have been analysed with a vertical cryomagnet at 235. Owing to the limited aperture of the cryomagnet, 50 unique magnetic reflections have been collected.

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Author contributions
M.G. grew the single crystals. Z.W. carried out the electric polarization, magnetostriction and magnetocapacitance experiments and data analysis. E.R. and N.Q. carried out the single-crystal neutron diffraction experiments and refined the magnetic structures. S.Z. and S.Y. provided the pulse field magnetization data. V.S. initiated the project and participated in all experiments. A.M. and V.S. wrote the manuscript with assistance from N.Q. and input from E.R. and S.Z. All authors contributed to the scientific discussion and edited the manuscript.

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