Anomalous lattice compression and magnetic ordering in CuO at high pressures: A structural study and first-principles calculations

D. P. Kozlenko,¹ K. Družbicki,^{1,2} S. E. Kichanov,¹ E. V. Lukin,¹ H.-P. Liermann,³ K. V. Glazyrin,³ and B. N. Savenko¹¹*Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (JINR), 141980 Dubna, Russia*²*Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*³*Photon Sciences, Deutsches Elektronen Synchrotron, D-22607 Hamburg, Germany*

(Received 29 August 2016; revised manuscript received 24 January 2017; published 17 February 2017)

The structural and magnetic properties of multiferroic CuO have been studied by means of neutron and x-ray powder diffraction at pressures up to 11 and 38 GPa, respectively, and by first-principles theoretical calculations. Anomalous lattice compression is observed, with enlargement of the lattice parameter a , reaching a maximum at $P = 13$ GPa, followed by its reduction at higher pressures. The lattice distortion of the monoclinic structure at high pressures is accompanied by a progressive change of the oxygen coordination around Cu atoms from the square fourfold towards the octahedral sixfold coordination. The pressure-induced evolution of the structural properties and electronic structure of CuO was successfully elucidated in the framework of full-electronic density functional theory calculations with range-separated HSE06, and meta-generalized gradient approximation hybrid M06 functionals. The antiferromagnetic (AFM) ground state with a propagation vector $q = (0.5, 0, -0.5)$ remains stable in the studied pressure range. From the obtained structural parameters, the pressure dependencies of the principal superexchange magnetic interactions were analyzed, and the pressure behavior of the Néel temperature as well as the magnetic transition temperature from the intermediate incommensurate AFM multiferroic state to the commensurate AFM ground state were evaluated. The estimated upper limit of the Néel temperature at $P = 38$ GPa is about 260 K, not supporting the previously predicted existence of the multiferroic phase at room temperature and high pressure.

DOI: [10.1103/PhysRevB.95.054115](https://doi.org/10.1103/PhysRevB.95.054115)

I. INTRODUCTION

The transition metal oxides demonstrate a rich variety of challenging physical phenomena, including high-temperature superconductivity, multiferroicity, colossal magnetoresistance, and charge and orbital ordering, which are currently the focus of extensive scientific research [1–4]. In particular, the layered cuprates, exhibiting the highest known critical superconducting temperatures (T_C) up to 138 K, have been thoroughly studied over last decades [4,5]. The simplest copper oxide sharing general structural features with the complicated structures of layered cuprates is a tenorite, CuO. The formation of the charge stripes, one of the key features characteristic for high- T_C superconductors, was revealed in CuO [6]. CuO is a charge transfer insulator, and it crystallizes in the monoclinic structure with $C2/c$ symmetry [7]. The long-range incommensurate spiral antiferromagnetic (AFM) state is formed in CuO at $T_N = 230$ K, followed by the first-order transition into the commensurate AFM state below $T_{N1} = 213$ K [8].

The recent discovery of ferroelectric polarization induced by the spiral magnetic order in the incommensurate AFM phase of CuO consigned this material as improperly multiferroic, with one of the highest ferroelectric transition temperatures known so far for this class of compounds [9]. Subsequent theoretical calculations predicted that the multiferroic incommensurate phase of CuO, existing only in a narrow temperature range 213–230 K at ambient pressure, can be stably extended into the ground state in the temperature domain from 0 to above 300 K at high pressures of 20–40 GPa [10]. However, these calculations were based on the experimental studies of the crystal and magnetic structures of CuO performed previously in limited pressure ranges up to

about 10 and 2 GPa, respectively [11,12]. More recently, a possible change of the magnetic order in CuO at $P \sim 4$ GPa was assumed from the high-pressure behavior of Raman spectra [13].

In this work, we explore the crystal and magnetic structure of CuO in the extended pressure range up to 38 and 11 GPa, respectively, by means of x-ray and neutron powder diffraction. We find that CuO demonstrates an anomalous lattice compression, resulting in the sign-reversal pressure behavior of the a lattice parameter and gradual modification of the oxygen coordination around Cu atoms from the square fourfold towards the octahedral sixfold coordination at $P \sim 12$ GPa. Extensive first-principles calculations are performed for the analysis of the observed structural anomalies in CuO as well as the evolution of the electronic structure. The structural data are used to explore the pressure behavior of the magnetically ordered states.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A commercially available powdered CuO sample of 99.9% purity was used in the experiments. The angle-dispersive x-ray powder diffraction (XRD) patterns at pressures up to 38 GPa and ambient temperature were measured at the Extreme Conditions Beamline [14] (P02.2, PETRA III, DESY, Germany) using a wavelength $\lambda = 0.29118$ Å. A BX90-type diamond anvil cell [15] was used for the XRD experiments. Diamonds with culets of 300 μm were used. The sample was loaded into a 150- μm -diameter hole made in the Re gasket indented to about 25 μm thickness. Neon gas loaded under pressure of ~ 0.15 GPa was used as a pressure-transmitting medium. The pressure was determined by the ruby fluorescence technique.

FIG. 1. Computational model of the monoclinic structure of CuO, representing simplified antiferromagnetic spin alignment of Cu ions (+/-), shown as blue spheres. The red spheres correspond to oxygen positions.

The two-dimensional XRD images were converted to one-dimensional diffraction patterns using the FIT2D program [16].

The neutron powder diffraction measurements at pressures up to 11 GPa were performed at selected temperatures in the range 4–290 K with DN-12 [17] and DN-6 diffractometers (IBR-2 pulsed reactor, Joint Institute for Nuclear Research [JINR], Russia). A sample with a volume of about 2 mm³ was loaded into the sapphire anvil high-pressure cell [18]. The diffraction patterns were collected at scattering angles of 90° and 45° with a resolution of $\Delta d/d = 0.015$ and 0.022, respectively. The data from the XRD and neutron powder diffraction experiments were analyzed by the Rietveld method using the FullProf program [19].

The density-functional theory (DFT) calculations were carried out in the spin-unrestricted formalism with the CRYSTAL14 code [20]. The initial model of the crystallographic and magnetic unit cell used in the calculations and visualized with the VESTA program [21] is presented in Fig. 1, referring to the monoclinic $C2/c$ structure and the lattice parameters $a = 4.680$, $b = 3.412$, $c = 5.108$ Å, and $\beta = 99.526^\circ$. Due to the large computational cost of the employed methodology, a simplified AFM arrangement of Cu spins was used ($Z = 4$), rather than a fully extended model with a propagation vector $q = (0.5, 0, -0.5)$, as proposed by Forsyth *et al.* [8].

The electronic orbitals were expanded as linear combinations of the atom-centered orbital (LCAO) Gaussian-type functions, with an exact treatment of the core electrons, i.e., without use of pseudopotentials. We employed the triple-zeta

valence with polarization quality (TZVP) full-electron basis set for copper according to Ruiz *et al.* [22], along with the def2-TZVP basis set for oxygen [23]. The self-consistent field (SCF) calculations were converged to a tolerance of 10^{-8} a.u. per unit cell, with a Monkhorst-Pack grid of $8 \times 8 \times 8$ points for the sampling of the reciprocal space. The truncation of the Coulomb and exchange sums in direct space was controlled by setting the Gaussian overlap set to $7 \times 7 \times 7 \times 9 \times 30$. The geometry optimization under external hydrostatic pressure was performed with the root-mean-square errors (RMS) for the energy gradients and maximal atomic displacements converged to 0.00025 a.u. and 0.0005 a.u., respectively.

The bond critical point analysis and the determination of atomic basins within the quantum theory of atoms in molecules (QTAIM) framework was done using the TOPOND code [24], providing grids of scalar properties, such as the electron localization function (ELF).

III. RESULTS AND DISCUSSION

A. First-principles modeling of the structural parameters of CuO: A survey of performance of hybrid exchange-correlation functionals

The previous first-principles studies of CuO at high pressure were focused on the analysis of multiferroic properties and magnetic interactions [10]. In addition, the possible existence of some new structural polymorphs at very high pressures (above 70 GPa) as well as relevant evolution of the Jahn-Teller structural distortions were also explored [25]. In the work by Rocquefelte *et al.* [10] and other relevant studies at ambient pressure [26,27], the Hubbard-corrected generalized gradient approximation (GGA+U) and local density approximation (LDA+U) calculations were performed by adding the on-site term to the Cu(3d) states. The authors were able to reasonably reproduce the total volume decrease at large pressure, but they did not report the evolution of the cell parameters and internal coordinates. Here, we refer to application of more robust hybrid exchange-correlation functionals.

Table I provides a survey for performance of several hybrid functionals selected to describe the structural parameters of CuO at ambient pressure [28–39]. For a comparison, the standard global hybrid functionals were used with the portion of the exact Hartree-Fock (HF) exchange varied from 16% to

TABLE I. The unit cell parameters of monoclinic CuO at ambient pressure from the synchrotron x-ray diffraction and according to the DFT/LCAO/TZVP calculations with different hybrid functionals.

XC	Type	a (Å)	b (Å)	c (Å)	β (deg.)	V (Å ³)
B1WC [28]	Hybrid (16% HF)	4.783	3.233	5.114	98.04	78.31
WC1LYP [29]		4.717	3.432	5.179	93.98	83.65
B3PW [30–32]	Hybrid (20% HF)	4.778	3.349	5.163	96.81	82.02
PBEsol0 [33–34]		4.799	3.186	5.084	100.30	76.49
PBE0 [33]	Hybrid (25% HF)	4.823	3.262	5.138	99.34	79.75
M06 [35]		4.712	3.425	5.158	96.99	82.62
HSE06 [36]	SR-hybrid	4.820	3.269	5.143	98.73	80.10
HISS [37–38]	MR-hybrid	4.828	3.210	5.107	100.60	77.81
wB97-X [39]	LR-hybrid	4.729	3.499	5.220	92.44	86.29
Present x-ray study		4.695	3.436	5.147	99.46	81.89

25%, and further extended to 27% with the meta-GGA hybrid M06 scheme. This comparison was extended to the range-separated hybrids, which evaluate the HF exchange only in the short-range (SR), middle-range (MR), or long-range (LR).

By inspection of Table I, it is clear that no dramatic difference can be found, since all the functionals were able to provide the absolute mean error of the cell parameters better than 3%. Interestingly, the meta-GGA hybrid M06 scheme gives an exceptionally low overall error of 1.0%. The Perdew-Burke-Ernzerhof (PBE)0 and Heyd-Scuseria-Ernzerhof (HSE)06 schemes, which can be treated as the most-standard hybrid functionals for solid-state calculations, act identically with an average error of 2%. Their similar performance suggests that the exact exchange is critical only at the short-range, since both functionals share the same founding of the PBE0 family [33].

B. Crystal structure at high pressure: Experiment and calculations

The XRD patterns of CuO, measured at selected pressures and ambient temperature, are shown in Fig. 2. They are consistent with the monoclinic $C2/c$ symmetry in the entire studied pressure range up to 38 GPa. The obtained pressure evolution of the unit cell volume is presented in Fig. 3, along with the results of first-principles calculations performed using

FIG. 2. X-ray diffraction patterns of CuO measured at selected pressures and ambient temperature, and refined by the Rietveld method. Experimental points and calculated profiles are shown. Tick marks at the bottom represent the calculated positions of diffraction peaks.

FIG. 3. The pressure variation of the unit cell volume in monoclinic CuO according to the synchrotron x-ray diffraction data and DFT/LCAO/TZVP calculations performed with different hybrid functionals. The GGA + U results (VASP) from Rocquefelte *et al.* Ref. [10] are also given for comparison.

the PBE0 family of hybrid functionals and the meta-GGA global hybrid (M06).

While the results of the M06 calculations match perfectly to the x-ray data, the HISS (Henderson – Izmaylov – Scuseria – Savin) and PBEsol0 calculations underestimate the unit cell volume. The GGA+U results by Rocquefelte *et al.* [10] also underestimate the unit cell volume, which becomes even more pronounced at higher pressures (Fig. 3). The PBEsol0 tends to overbind the CuO structure, as it was simply optimized in terms of the exchange enhancement factor, $F_x(s)$, in order to avoid a repulsive nature of the standard semilocal GGA. Taking this into account, the HSE06 and M06 functionals were selected for further modeling of the structural and electronic properties of CuO at high-pressure conditions.

The experimental volume compression data were fitted by the third-order Birch-Murnaghan equation of state [40]. The obtained bulk modulus [$B_0 = -V(dP/dV)_T$] and its pressure derivative [$B' = (dB_0/dP)_T$], $B_0 = 88(5)$ GPa and $B' = 7.5(8)$, are comparable with values previously obtained in the limited pressure range up to 9 GPa [11,41].

The lattice compression of CuO demonstrates an anomalous character (Fig. 4). The a lattice parameter exhibits expansion at moderate pressures, reaching the maximal value at $P \approx 13$ GPa and decreasing at higher pressures. After subsequent compression, its resulting value at $P = 38$ GPa, $a = 4.6966(2)$ Å, becomes about the same as the initial value at ambient pressure, $4.6948(1)$ Å. The same trend has been properly reproduced with calculations using both the HSE06 and M06 functionals (Fig. 4). In the former case, the expansion is predicted up to 7 GPa, while in the latter case, it is predicted up to 15 GPa.

The shortest b lattice parameter is the most compressible, with average compressibility [$k_i = -(1/a_{i0})(da_i/dP)_T$] $k_b = 0.0034$ GPa $^{-1}$, while that of the c parameter is about three times smaller, $k_c = 0.0012$ GPa $^{-1}$. The monoclinic angle β increases nonlinearly from 99.46° to 105.23° in the

FIG. 4. The lattice parameters and monoclinic angle of CuO as functions of pressure according to synchrotron x-ray measurements and theoretical calculations with the HSE06 and M06 functionals. The neutron powder diffraction data (NPD) from Ehrenberg *et al.* Ref. [11] are given for comparison. The lines are guides to the eye only.

studied pressure range, with a pronounced change in the average pressure coefficient in the pressure region $P \sim 13$ GPa, corresponding to the maximum in the pressure dependence of the a lattice parameter (Fig. 4).

The neutron diffraction patterns of CuO, measured at selected pressures up to 11 GPa and temperatures 10 and 290 K, are shown in Fig. 5. In the monoclinic crystal structure of CuO, the oxygen atoms located at $4(e)$ sites ($0 y 1/4$) form

FIG. 5. The neutron diffraction patterns of CuO, measured at selected pressures up to 11 GPa and temperatures 10 and 290 K at scattering angles 90° and 45° (inset), and processed by the Rietveld method. The experimental points and calculated profiles are shown. The ticks below represent calculated positions of the nuclear peaks. The characteristic magnetic peak of the AFM ground state with $q = (1/2, 0, -1/2)$ is marked as “AFM” in the inset.

nearly square planes around Cu atoms located at $4(c)$ sites ($1/4 1/4 0$), containing crossing $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ zigzag chains oriented along the $[10-1]$ and $[101]$ crystallographic directions (Fig. 6).

The oxygen coordinate y as a function of pressure, determined from the Rietveld refinements of the neutron diffraction data at $T = 10$ K, is shown in Fig. 7. The obtained values of the Cu–O bonds located in the square planes are very close; their difference is less than 1% in the studied pressure range. The nearest-neighbor copper atoms form a regular tetrahedron around the oxygen atoms. Therefore, about the same values of the Cu–O bonds point to the locations of the O atoms practically in the geometrical center of this tetrahedron (Fig. 6).

FIG. 6. (a) The monoclinic crystal structure of CuO. The fourfold coordinated Cu–O planes and tetrahedral coordination of Cu atoms around O atoms are shown. The two longest additional Cu–O distances are presented as dashed lines. (b) Schematic representation of the Cu–O–Cu zigzag chains oriented along the $[10-1]$ and $[101]$ crystallographic directions, with geometry of interatomic angles and relevant superexchange interactions.

FIG. 7. The pressure dependencies of the oxygen coordinate y (a), Cu–O bond distances (b), and intrachain (c) and interchain (d) Cu–O–Cu bond angles. The errors are within the symbol sizes. The squares show experimental results from the present neutron data, triangles show neutron data [Ref. [11]], and circles indicate calculated results from present x-ray data. The results of the first-principles calculations under pressure (HSE06; M06) are given as dashed lines.

This confinement easily enables calculation of the oxygen coordinate y from copper positions with fixed coordinates in the extended pressure range up to 38 GPa from the XRD data, although it is much less sensitive for direct accurate determination of light oxygen atoms positions. One should also note that the y value has very weak temperature variation not exceeding 0.5% in the considered temperature range [42]. Both the calculated and experimental positions of oxygen coordinates as well as average Cu–O bonds in square planes as functions of pressure are in very good agreement (Fig. 6). These Cu–O bonds are weakly modified by pressure and have compressibility $k = 0.0005 \text{ GPa}^{-1}$.

The monoclinic $C2/c$ structure of CuO is a highly distorted analogue of the face-centered NaCl-type cubic structure, typical for relevant transition metal oxides such as MnO, FeO, and NiO and characterized by the octahedral oxygen coordination of transition metal ions. The peculiar structure of CuO has been attributed to a Jahn-Teller-like distortion caused by the unpaired d electron, which is also related to the magnetic moments and band structure of CuO [7,43].

Due to the high distortion in CuO, there are two additional Cu–O distances, the values of which at ambient pressure are 2.79 Å, i.e., about 1.5 times longer in comparison with the nearest-neighbor bonds in square planes (Fig. 6). The longer Cu–O distances are strongly compressed in the moderate pressure range up to about 10 GPa, with compressibility $k_1 = 0.01 \text{ GPa}^{-1}$, i.e., twenty times larger in comparison with the value for the bonds forming square planes. This is, hence, a pathway of internal compression in CuO at lower pressures, and it clearly demonstrates that chemical bonding between these involved Cu and O atoms is either absent or very weak.

At pressures above 10 GPa, the compressibility of the longer Cu–O distances is reduced significantly to $k_1 = 0.003 \text{ GPa}^{-1}$, and it evolves further similarly to the square-planar bonds. The values of these distances at 38 GPa, 2.27 Å, become comparable with those of Cu–O bonds in square planes of 1.92 Å, with a relative difference of only 15%. This provides evidence for a change of the nearest-neighbor oxygen coordination around copper atoms from the fourfold square to the sixfold octahedral coordination in the monoclinic crystal structure of CuO at $P > 13 \text{ GPa}$. The observed anomalies in pressure behavior of the a lattice parameter and the β monoclinic angle may be associated with the isostructural phase transformation, caused by the modification of the oxygen coordination and the involved chemical bond strengths.

The calculations with the HSE06 and M06 functionals reproduce the characteristic features of the pressure behavior of structural parameters of CuO (Fig. 7). In addition, they predict some splitting between the in-plane Cu–O bonds, which is somewhat overestimated in comparison with the previous [11] and present experimental data, and it is enhanced upon compression. Nevertheless, this splitting remains quite small and reaches a value of only about 2% in the studied pressure range up to 38 GPa, generally supporting the approach to the treatment of experimental data proposed here.

C. Electronic structure under pressure

To shed more light on the character of the CuO bonding, we employed topological analysis of the electron density in terms of Bader's quantum theory of atoms in molecules [44] (QTAIM), further supported by ELF analysis [45]. We

FIG. 8. (Left) The pressure-induced changes in the Laplacian of electron density at the bond critical points defining the short (x,y) and long (z) Cu–O bonds as derived from the QTAIM analysis. (Right) The ELF surface ($s = 0.76$) for CuO at two extreme pressure conditions studied.

refer here to the HSE06 results (see Fig. 8), for the sake of consistency with the most popular computational approaches used in the literature (i.e., due to the Vienna *Ab initio* Simulation Package [VASP] implementation).

The QTAIM analysis identifies clearly the (3,−1) type critical points associated with three different Cu–O bonds in a hypothetical octahedra: the short square-plane (x,y) and long-axis (z) points. The charge transfer in the direction of the oxygen nuclei dominates here, and the electron density $\rho(r)$ is therefore more concentrated in the atomic basins. Such interaction is typical for the closed-shell bonds in ionic crystals. The ionic nature of the analyzed bonds is evidenced from the analysis of the Laplacian of the electron density $\nabla^2\rho$ scalar field. Since $\nabla^2\rho > 0$ in each case, depletion of the electronic distribution is found.

The pressure behavior of the Laplacian of the electron density demonstrates nearly linear enlargement with slight modifications of the slope for the shorter in-plane (x,y) and the long out-of-plane (z) Cu–O distances at $P \sim 12$ GPa, corresponding to the observed structural anomalies. The relevant Laplacian value for the long Cu–O distance is about an order of magnitude smaller with respect to those corresponding to the short Cu–O bonds at ambient pressure. This relative difference is reduced more than three times upon compression up to 38 GPa. It implies a pronounced strengthening of the chemical bonds corresponding to the long Cu–O distances and supports a pressure-induced change from the fourfold to the sixfold oxygen coordination in CuO.

The results of the ELF analysis are presented on the right panel of Fig. 8. The ELF can be essentially defined as electron localization index mapping of the inverse probability of finding two electrons with the same spin at a given point in space. The presented isosurfaces clearly confirm the transfer of electrons into the oxygen shells. While covalent bonds must correspond to the ELF maxima located between the ions, the closed shells are here separated by ELF minima. In this case, the interactions are clearly ionic. The considerably distorted shape of the ELF spheres remains constant all the way through. There is no qualitative difference in their curvature when comparing the zero-pressure and 37.5 GPa data, which confirms further that the ionic bonding character in CuO does not change in the studied pressure range.

In addition to the ELF analysis, the density of electronic states (DOS) was also followed with pressure (Fig. 9). Initial calculations performed for the simplified spin arrangement model with $Z = 4$, used all throughout this work, revealed some differences in comparison with the results obtained for the experimentally observed spin arrangement model with $Z = 8$ by Rödl *et al.* (compared to calculations by the HSE06 with the short-range HF exchange fraction $\alpha = 0.25$ therein) [46]. Particularly, the simplified model with $Z = 4$ results in an unoccupied $d(x^2 - y^2)$ state with a less pronounced peak, which is spread over a wider energy range and results in a reduced band gap of 1.9 eV compared to that of about 3.1 eV for the $Z = 8$ model. Due to this, additional calculations for the AFM spin arrangement model with $Z = 8$ were also performed (Fig. 9) for pressure values of 0 and 37.5 GPa.

FIG. 9. The pressure dependence of the density of electronic states (DOS) in antiferromagnetic CuO at $P = 0$ and 37.5 GPa, according to the CRYSTAL14/HSE06/TZVP calculations for the $Z = 8$ AFM spin arrangement. The contributions from the e_g and t_{2g} states of Cu ($3d$) are projected using the local coordinate system centered on Cu, where the x and y axes are directed approximately to four neighboring oxygen atoms. The top of the valence band is aligned to 0 eV.

Application of high pressure leads to more pronounced changes in the density of e_g states. The peak in the unoccupied minority spin $x^2 - y^2$ states in the conduction band becomes more pronounced due to its narrowing, while another characteristic peak in the majority spin $x^2 - y^2$ states located at the bottom of the valence band, in contrast, noticeably broadens over a larger energy range (Fig. 9). The $x^2 - y^2$ states were also found to strongly hybridize with $2p$ oxygen orbitals, consistent with Ref. [46]. The shortening of the apical-like Cu–O bonds upon pressure also results in an increase of the z^2 contributions in the valence regime, but it still does not change the nature of the valence state. The DOS behavior reflects no principal changes in the character of the Jahn-Teller structural distortions in CuO in the studied pressure range, as also supported by the experimental and calculated data upon pressure modification of the Cu–O distances. At the studied pressure range, the theoretical band gap lowers by no more than 0.3 eV.

D. Magnetic ordering

In the neutron diffraction patterns, measured at ambient pressure, appearance of the magnetic peak ($\pm q_x, 0, \pm q_z$) at $d \approx 7.38 \text{ \AA}$ was observed below $T_N \approx 230 \text{ K}$ (Fig. 5), corresponding to formation of the AFM state with propagation vector $q = (q_x, 0, q_z)$. The components of the propagation vector were found to be incommensurate, $q_x = 0.505$ and $q_z = -0.487$, in the temperature range 215–230 K and commensurate, $q_x = -q_z = 0.5$, for temperatures below 215 K, in accordance with earlier studies [8,12]. The obtained value of the Cu ordered magnetic moment at $T = 10 \text{ K}$ is $\mu = 0.85(5)\mu_B$, which is comparable with values reported previously, i.e., 0.65–0.69 μ_B [8,47]. From the analysis of the neutron diffraction data, it was found that the commensurate AFM phase remains in the ground state at low temperatures in the studied pressure range up to 11 GPa.

The principal magnetic interactions responsible for the observed symmetry of the magnetic ground state in CuO are superexchange interactions in crossing Cu–O–Cu chains, containing antiferromagnetically coupled Cu magnetic moments with spins $S = 1/2$ along the $[10-1]$ direction and ferromagnetically coupled moments along the $[101]$ direction (Fig. 6). The superexchange in the Cu–O–Cu chains along the $[10-1]$ direction is the principal AFM magnetic interaction. Its relatively large absolute value, $J \approx 67\text{--}80 \text{ meV}$ [47,48,49], is responsible for the high magnetic ordering temperature $T_N = 230 \text{ K}$. The superexchange in the Cu–O–Cu chains along the $[101]$ direction was found to be weakly ferromagnetic (FM), with the absolute value $J_1 \approx 5 \text{ meV}$ [48,49]. An interplay of these AFM and FM interactions is likely responsible for appearance of the intermediate incommensurate AFM phase in CuO [9,12]. The strong anisotropy of magnetic interactions with $J/J_1 \approx 16$ results in the quasi-one-dimensional behavior of the magnetic properties of CuO [50]. An important role of the second-neighbor superexchange interactions J_2 between Cu–O–Cu chains along the $[10-1]$ direction has also been pointed out [10,43]. These interchain interactions are rather weak and comparable in magnitude with J_1 .

In a theoretical study [51], the relationships among the Néel temperature (T_N) and intrachain (J) and interchain (J_2) magnetic couplings for a quasi-one-dimensional Heisenberg

antiferromagnet were calculated using Monte Carlo simulations and random phase approximation (RPA) as:

$$J_2 = T_N / \left[4c \sqrt{\ln\left(\frac{\lambda J}{T_N}\right) + \frac{1}{2} \ln\ln\left(\frac{\lambda J}{T_N}\right)} \right], \quad (1)$$

where constants values are $c = 0.233$ and $\lambda = 2.6$.

Taking the values of the dominant intrachain magnetic coupling $J = 67 \text{ meV}$ and $T_N = 230 \text{ K}$, the magnitude of the interchain coupling is evaluated as $J_2 = 13.4 \text{ meV}$. This value is comparable with that previously calculated at ambient pressure, i.e., 20 meV [10,43].

The strength of superexchange interactions in cuprates has a direct relationship with the variation of the Cu–O–Cu bond angles (φ), while it is nearly independent of variation in the Cu–O distances [8,50]. The Cu–O–Cu superexchange strength decreases gradually on departure of the bond angle from 180° , and it changes character from AFM to FM approaching the $\varphi = 90^\circ$ limit.

The pressure dependencies of the intra- and interchain Cu–O–Cu bond angles obtained from the neutron and XRD data are shown in Fig. 7 along with the values provided by the HSE06 and M06 calculations. The φ_{10-1} angle mediating the strongest intrachain AFM superexchange interactions exhibits the largest pressure variation, and it increases from 146.2° to 165.5° in the pressure range 0–38 GPa. Another intrachain angle, φ_{101} , mediating weaker FM superexchange interactions, decreases much more slowly from 108.4° to 98.6° . The interchain bond angles also demonstrate weak reduction upon compression up to 38 GPa: φ_{ic1} decreases from 104° to 96° , and φ_{ic2} decreases from 95.6° to 92.7° . The first-principles calculations reproduce qualitatively the experimentally observed trends in pressure behavior of the intra- and interchain angles. In particular, calculations with the HSE06 functional describe more precisely the pressure dependencies of the φ_{10-1} , φ_{101} , and φ_{ic2} angles, while calculations with the M06 functional provide better description of the pressure dependence of the φ_{ic1} angle (Fig. 7).

Using the experimental dependencies of the Cu–O–Cu bond angles, it is possible to evaluate the pressure dependence of the Néel temperature using the expression in Eq. (1). In the calculation procedure, the empirical relationship between the superexchange interaction strength and the Cu–O–Cu bond angle, derived in Refs. [8,50], was used to determine the pressure dependence of the dominant intrachain magnetic coupling J . The main contribution to the interchain magnetic coupling is given by the second-neighbor superexchange interaction J_2 , mediated by the φ_{ic2} bond angle. The weak pressure dependence of this angle (Fig. 7) allows us to neglect the pressure variation of this magnetic coupling in the considered pressure range, keeping it as the constant evaluated at ambient pressure, $J_2 = 13.4 \text{ meV}$. This assumption is consistent with the theoretical calculations [10], which evidenced weak modification of this J_2 magnetic coupling in the considered pressure range.

The calculated pressure dependence of the Néel temperature (Fig. 10) exhibits a nonlinear increase with a pressure coefficient $dT_N/dP \approx 2.4 \text{ K GPa}^{-1}$ at moderate pressures, which decreases noticeably to about 0.3 K GPa^{-1} at pressures above 10 GPa. Such behavior is a consequence of the pressure

FIG. 10. (a) The experimental and calculated pressure dependencies of the Néel temperature of CuO. The triangles are experimental points derived from the neutron diffraction measurements. The solid curves represent calculations with the parameters $c = 0.233$ and $\lambda = 2.6$ (green line), and $c = 0.274$ and $\lambda = 1.5$ (brown line). The red dashed line indicates calculation by Rocquefelte *et al.* Ref. [10]. (b), (c) The experimental temperature dependencies of the monoclinic angle of CuO at $P = 0$ (b) and 11 GPa (c).

variation of the φ_{10-1} bond angle, demonstrating a similar saturation trend (Fig. 7). As a result, the calculated T_N value is about 253 K at $P = 38$ GPa. It remains far below ambient temperature, in contrast to the theoretical predictions [10], based on the structural data measured in the limited pressure range below 10 GPa. The present evaluation of the pressure coefficient dT_N/dP at moderate pressures is consistent with the value 2.8 K GPa^{-1} , as determined in previous neutron scattering experiments for the pressure range up to 1.8 GPa [12]. Due to the small value of the ordered Cu magnetic moment, it is difficult to evaluate directly the pressure behavior of the magnetic transition temperature from its temperature variation using the neutron diffraction data. Nevertheless, the T_N and T_{N1} values can be associated with the peculiarities in the temperature dependencies of the monoclinic angle (Fig. 10) caused by the magnetolattice coupling effects [42]. An increase of the Néel temperature T_N from 230 to about 250 K (Fig. 10) and a decrease of the transition temperature T_{N1} from the intermediate incommensurate to the commensurate AFM ground state from 215 to about 190 K are estimated for the pressure range 0–11 GPa. The corresponding pressure coefficients $dT_N/dP \approx 1.8 \text{ K GPa}^{-1}$ and $dT_{N1}/dP \approx -2.3 \text{ K GPa}^{-1}$ are comparable with ones derived from the calculated pressure dependence of the Néel temperature above and experimental data obtained in the restricted pressure range up to 1.8 GPa [12]. A comparison

shows that the calculation procedure based on Eq. (1) with coefficients $c = 0.233$ and $\lambda = 2.6$ from Ref. 52 somewhat underestimates the T_N value (Fig. 10). Considering these coefficients as the variable parameters in the fitting procedure, the experimentally determined pressure dependence of the Néel temperature can be described satisfactorily by Eq. (1) with values $c = 0.274$ and $\lambda = 1.5$ (Fig. 10). Nevertheless, the estimated value $T_N \approx 262 \text{ K}$ at $P = 38 \text{ GPa}$ in this modified approach still remains noticeably below ambient temperature.

IV. CONCLUSIONS

The present results demonstrate that the copper oxide CuO undergoes an anomalous lattice compression. It is associated with the isostructural phase transformation, leading to a change of the oxygen coordination around Cu atoms from the square fourfold to the octahedral sixfold coordination. State-of-the-art first-principles calculations based on the application of the modern hybrid-DFT HSE06 and M06 approaches were employed with high accuracy, providing successful description of the pressure evolution of the structural parameters and the electronic structure of the monoclinic CuO.

The application of high pressure leads to a significant increase of the Cu–O–Cu bond angle, mediating the strength of the dominant AFM superexchange interactions in the zigzag chains oriented along the $[10-1]$ direction. The in-plane Cu–O bond lengths and the rest of the Cu–O–Cu intrachain and interchain bond angles exhibit a less-pronounced decrease upon compression. The commensurate AFM ground state remains stable, and the transition temperature to the intermediate incommensurate multiferroic AFM state decreases from 215 to about 190 K in the pressure range 0–11 GPa. The calculated pressure dependence of the Néel temperature demonstrates a saturation trend at pressures above 20 GPa, and it reaches a value of $T_N \sim 260 \text{ K}$ at $P = 38 \text{ GPa}$. This implies that the temperature region corresponding to the incommensurate multiferroic phase is extended under pressure, but it likely remains far below ambient temperature in the studied pressure range up to 38 GPa.

ACKNOWLEDGMENTS

This research was supported by the Russian Foundation for Basic Research, Grant No. 15-02-03248, and in part by PL-Grid Infrastructure (Grant IDs: solidstate2015; latticedynamics02). The financial support of the Polish Government Plenipotentiary for JINR in Dubna (Grant No. 46/9/22.01.2016) is gratefully acknowledged. K.D. kindly thanks Wei Wu (University College London, UK) and Pablo Riviero (Louisiana State University, US) for their kind help with the CRYSTAL14 calculations.

- [1] S.-W. Cheong, *Nature Mater.* **6**, 927 (2007).
- [2] M. A. Kastner, R. J. Birgeneau, G. Shirane, and Y. Endoh, *Rev. Mod. Phys.* **70**, 897 (1998).
- [3] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, *Nature* **426**, 55 (2003).

- [4] N. Plakida, *High-Temperature Cuprate Superconductors: Experiment, Theory and Applications* (Springer, New York, 2010).
- [5] K. A. Lokshin, D. A. Pavlov, S. N. Putilin, E. V. Antipov, D. V. Sheptyakov, and A. M. Balagurov, *Phys. Rev. B* **63**, 064511 (2001).

- [6] X. G. Zheng, C. N. Xu, Y. Tomokiyo, E. Tanaka, H. Yamada, and Y. Soejima, *Phys. Rev. Lett.* **85**, 5170 (2000).
- [7] S. Åsbrink and L.-J. Norrby, *Acta Crystallogr. B* **26**, 8 (1970).
- [8] J. B. Forsyth, P. J. Brown, and B. M. Wanklyn, *J. Phys. C* **21**, 2917 (1989).
- [9] T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist, and A. P. Ramirez, *Nature Mater.* **7**, 291 (2008).
- [10] X. Rocquefelte, K. Schwarz, P. Blaha, S. Kumar, and J. van den Brink, *Nature Commun.* **4**, 2511 (2013).
- [11] H. Ehrenberg, J. A. McAllister, W. G. Marshall, and J. P. Attfield, *J. Phys.: Condens. Matter* **11**, 6501 (1999).
- [12] T. Chatterji, P. J. Brown, and J. B. Forsyth, *J. Phys.: Condens. Matter* **17**, S3057 (2005).
- [13] R. Jana, P. Saha, V. Pareek, A. Basu, S. Kapri, S. Bhattacharyya, and G. D. Mukherjee, *Sci. Rep.* **6**, 31610 (2016).
- [14] H.-P. Liermann, W. Morgenroth, A. Ehnes, A. Berghäuser, B. Winkler, H. Franz, and E. Weckert, *J. Phys.: Conf. Ser.* **215**, 012029 (2010).
- [15] N. A. Dubrovinskaya and L. S. Dubrovinsky, *Rev. Sci. Instrum.* **74**, 3433 (2003).
- [16] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Häusermann, *High Press. Res.* **14**, 235 (1996).
- [17] V. L. Aksenov, A. M. Balagurov, V. P. Glazkov, D. P. Kozlenko, I. V. Naumov, B. N. Savenko, D. V. Sheptyakov, V. A. Somenkov, A. P. Bulkin, V. A. Kudryashev, and V. A. Trounov, *Physica B* **265**, 258 (1999).
- [18] V. P. Glazkov and I. N. Goncharenko, *Fizika I Tekhnika Vysokih Davlenij* **1**, 56 (1991) (in Russian).
- [19] J. Rodríguez-Carvajal, *Physica B* **192**, 55 (1993).
- [20] R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noël, M. Causà, M. Rérat, and B. Kirtman, *Int. J. Quantum Chem.* **114**, 1287 (2014).
- [21] K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- [22] E. Ruiz, M. Llunell, and P. Alemany, *J. Solid State Chem.* **176**, 400 (2003).
- [23] B. Civalleri, D. Presti, R. Dovesi, and A. Savin, On choosing the best density functional approximation, in *Chemical Modelling: Application and Theory*, Vol. 9, edited by M. Springborg (RSC Publishing, London, 2012), p. 168.
- [24] C. Gatti, V. R. Saunders, and C. Roetti, *J. Chem. Phys.* **101**, 10686 (1994).
- [25] M. J. Greschner, N. Chen, and Y. Yao, *J. Phys.: Condens. Matter* **28**, 025401 (2016).
- [26] C. Gattinoni and A. Michaelides, *Surf. Sci. Rep.* **70**, 424 (2015).
- [27] M. Heinemann, B. Eifert, and C. Heiliger, *Phys. Rev. B* **87**, 115111 (2013).
- [28] D. I. Bilc, R. Orlando, R. Shaltaf, G.-M. Rignanese, J. Íñiguez, and Ph. Ghosez, *Phys. Rev. B* **77**, 165107 (2008).
- [29] R. Demichelis, B. Civalleri, M. Ferrabone, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 406 (2010).
- [30] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [31] J. P. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8800 (1986).
- [32] J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- [33] C. Adamo and V. Barone, *J. Chem. Phys.* **110**, 6158 (1999).
- [34] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [35] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* **120**, 215 (2008).
- [36] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *J. Chem. Phys.* **125**, 224106 (2006).
- [37] T. M. Henderson, A. F. Izmaylov, G. E. Scuseria, and A. Savin, *J. Chem. Phys.* **127**, 221103 (2007).
- [38] T. M. Henderson, A. F. Izmaylov, G. E. Scuseria, and A. Savin, *J. Chem. Theory Comput.* **4**, 1254 (2008).
- [39] J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.* **128**, 084106 (2008).
- [40] F. J. Birch, *J. Geophys. Res.* **91**, 4949 (1986).
- [41] M. Malinowski, S. Åsbrink, and A. Kvick, *High Press. Res.* **4**, 429 (1990).
- [42] H. Yamada, X. G. Zheng, Y. Soejima, and M. Kawaminami, *Phys. Rev. B* **69**, 104104 (2004).
- [43] A. Filippetti and V. Fiorentini, *Phys. Rev. Lett.* **95**, 086405 (2005).
- [44] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford University Press, Oxford, 1990).
- [45] A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* **92**, 5397 (1990).
- [46] C. Rödl, F. Sottile, and L. Reining, *Phys. Rev. B* **91**, 045102 (2015).
- [47] B. X. Yang, T. R. Thurston, J. M. Tranquada, and G. Shirane, *Phys. Rev. B* **39**, 4343 (1989).
- [48] M. Aïn, W. Reichardt, B. Hennion, G. Pepy, and B. M. Wanklyn, *Physica C* **162**, 1279 (1989).
- [49] A. T. Boothroyd, A. Mukherjee, S. Fulton, T. G. Perring, R. S. Eccleston, H. A. Mook, and B. M. Wanklyn, *Physica B* **234–236**, 731 (1997).
- [50] T. Shimizu, T. Matsumoto, A. Goto, T. V. Chandrasekhar Rao, K. Yoshimura, and K. Kosuge, *Phys. Rev. B* **68**, 224433 (2003).
- [51] C. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, M. Troyer, and H. Takayama, *Phys. Rev. Lett.* **94**, 217201 (2005).