

## Room-temperature structural phase transition in the quasi-2D spin- $\frac{1}{2}$ Heisenberg antiferromagnet $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$

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$\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  (with pz denoting pyrazine,  $\text{C}_4\text{H}_4\text{N}_2$ ) is a two-dimensional spin-1/2 square-lattice antiferromagnet with  $T_N = 4.24$  K. Due to a persisting focus on the low-temperature magnetic properties, its room-temperature structural and physical properties caught no attention up to now. Here we report a study of the structural features of  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  in the paramagnetic phase, up to 330 K. By employing magnetization, specific heat,  $^{35}\text{Cl}$  nuclear magnetic resonance, and neutron diffraction measurements, we provide evidence of a second-order phase transition at  $T^* = 294$  K, not reported before. The absence of a magnetic ordering across  $T^*$  in the magnetization data, yet the presence of a sizable anomaly in the specific heat, suggests a structural order-to-disorder-type transition. NMR and neutron-diffraction data corroborate our conjecture by revealing subtle angular distortions of the pyrazine rings and of  $\text{ClO}_4^-$  counteranion tetrahedra, shown to adopt a configuration of higher symmetry above the transition temperature.

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### I. INTRODUCTION

As a notable physical realization of a quasi-two-dimensional (quasi-2D) Heisenberg antiferromagnet,  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  has been a test case for investigating the competition between long-range magnetic order and quantum fluctuations [1,2]. Its structure consists of stacks along the  $c$  axis of well-isolated nearly square layers of  $\text{Cu}^{2+}$  ions in the  $ab$  plane, rotated by  $45^\circ$  with respect to the in-plane primitive vectors, as shown schematically in Fig. 1. Along the  $c$  axis, each layer is shifted by half a unit cell along the  $a$  and  $b$  axes. Each  $\text{Cu}^{2+}$  ion is bridged to its four nearest neighbors (NNs) by  $\text{C}_4\text{H}_4\text{N}_2$  pyrazine ligands, which provide the intralayer superexchange interaction. Two  $\text{ClO}_4^-$  perchlorate counteranions, linked to  $\text{Cu}^{2+}$  ions via one of the oxygen atoms in the  $\text{O}_4$  tetrahedra, provide a sufficient interlayer separation along the  $c$  axis, hence implying a negligible interlayer interaction. Overall, this results in a  $\text{Cu}^{2+}$ -ion arrangement of nearly tetragonal symmetry [3]. The three-dimensional (3D) antiferromagnetism of  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  has been extensively studied by inelastic neutron scattering (INS) [4], muon-spin rotation ( $\mu\text{SR}$ ) [5], and nuclear magnetic resonance (NMR) [6] measurements. It has also been shown that applied magnetic fields along the  $c$  axis strengthen the antiferromagnetic (AFM) order by suppressing the quantum fluctuations, hence enhancing  $T_N$  above its zero-field value of 4.24 K [4]. On the other hand, external hydrostatic pressure reduces  $T_N$  [6], most likely by enforcing the one-dimensional (1D)-type

interactions [7], as suggested by results of density-functional theory (DFT) calculations on similar compounds [8,9].

The crystal structure of  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  was determined at 163 and 293 K from single-crystal x-ray diffraction data [10], obtaining a better refinement with the  $C2/c$  space group in the first case and with the  $C2/m$  space group in the latter. It was also observed that the four pyrazine moieties form two sets at low temperature, each of them characterized by a different tilting angle with respect to the  $ab$  plane. The values of these angles are distinct at 163 K, but they become identical ( $65.8^\circ$ ) at 293 K. Along with x-ray diffraction patterns, Choi *et al.* [2] reported also infrared-spectroscopy data, used to track the evolution of the vibrational modes as a function of temperature. Upon heating, the latter measurements indicated a softening of the vibrational modes, related to the out-of-plane deformations of the pyrazine rings starting at approximately 180 K.

In this work, by combining data from NMR, specific-heat, and neutron-diffraction experiments, we provide clear evidence for a *structural phase transition* occurring at  $T^* = 294(1)$  K, not reported before in the literature. Our results indicate that the two initially different Cl sites become equivalent above  $T^*$  and that the symmetry of the individual pyrazine rings increases upon heating above  $T^*$ .

After introducing the experimental details in Sec. II, in Secs. III A and III B, we describe the material characterization via magnetization and specific-heat measurements. From these data, we identify the onset of the AFM order at  $T_N$  and of the structural transition at  $T^*$ , respectively. The  $^{35}\text{Cl}$  NMR results discussed in Sec. III C clearly show the merging of the two lines upon heating, reflecting an increase in structure symmetry and allowing for an evaluation of the isotropic hyperfine coupling. Finally, to precisely identify the

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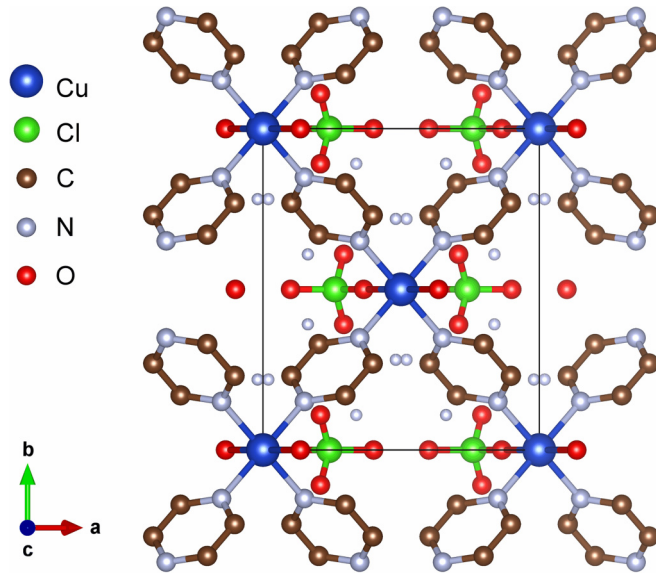


FIG. 1. A layer of  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$ , whose  $C2/m$  structure (space group no. 12) was determined from neutron-diffraction data at 294 K. Each  $\text{Cu}(\text{II})$  atom (blue) is linked via pyrazine rings (C = brown, N = gray) to four other copper ions, all lying in the  $ab$  plane. The layers are spaced by perchlorate counteranions (Cl = green, O = red), lying along the interlayer  $c$ -axis direction. As described in the text and in Table I (see the Appendix), the N and C atoms in the pyrazine rings and the O atoms in the perchlorate counteranions have different Wyckoff positions. Each counteranion contains a Cl site at the center and four O atoms at its vertices.

variations in bond lengths and angles, we employed neutron powder diffraction measurements, whose results are reported in Sec. III D. The combined data of our investigations indicate that the second-order structural transition is accompanied by subtle transformations in both the  $\text{ClO}_4^-$  tetrahedra and the  $\text{C}_4\text{H}_4\text{N}_2$  pyrazine ligands.

## II. EXPERIMENTAL DETAILS

The  $\text{Cu}(\text{ClO}_4)_2$  crystals were synthesized by dissolving  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and pyrazine in water with a drop of dilute  $\text{HClO}_4(\text{aq})$ , in order to prevent the precipitation of  $\text{Cu}(\text{OH})_2$  and of  $\text{CuCO}_3$ . The solution was then partially covered and left to evaporate slowly, with the crystals growing over several weeks. Finally, the mixture was filtered, the recovered crystals were washed in deionized water at  $\sim 10^\circ\text{C}$ , and dried in air. Since the samples are hygroscopic, they were stored in an inert-gas atmosphere [10]. Single crystals with a typical mass of  $\sim 80$  mg were aligned with the  $c$  axis (*hard* axis) parallel to the applied magnetic field, for both the magnetization and NMR experiments. Given the easily identifiable  $ab$  planes, delimited by smooth surfaces, the visual crystal alignment was achieved with an uncertainty of about  $5^\circ$ . For the neutron-diffraction measurements, we used deuterated powder synthesized by following the same protocol, but employing deuterated reagents. The magnetization measurements were performed with a commercial magnetic property measurement system (MPMS) XL setup from 2 to 310 K in an applied magnetic field of 5 mT. The heat-capacity data were

collected by means of a Quantum Design physical property measurement system (PPMS-9 T) by using the relaxation method, both upon heating and upon cooling, in a temperature range between 250 and 330 K.

The  $^{35}\text{Cl}$ -NMR study comprised line-shape and spin-lattice relaxation time measurements in a 7.063-T field, corresponding to a Larmor frequency of 29.4664 MHz for the spin- $3/2$   $^{35}\text{Cl}$  quadrupolar nuclei. NMR signals were detected by employing a standard spin-echo sequence, consisting of  $\pi/2$  and  $\pi$  pulses of 2 and 4  $\mu\text{s}$ , respectively, with recycle delays ranging from 0.6 to 0.2 s for temperatures in the 4–310 K range. The NMR line shapes were obtained from fast Fourier transforms (FFTs) of the echo signals. The spin-lattice relaxation times  $T_1$  were measured via the inversion-recovery method using a  $\pi$ - $\pi/2$ - $\pi$  pulse sequence.

Neutron-diffraction experiments were performed at the HRPT diffractometer (high-resolution powder diffractometer for thermal neutrons) at the SINQ facility of the Paul Scherrer Institute (PSI) in Villigen, Switzerland. Several patterns were recorded between 260 and 330 K, using two different wavelengths ( $\lambda = 1.494$  and  $1.886$  Å) of the high-intensity mode (24' primary-beam collimation) [11]. The sample was placed in an 8-mm-diameter vanadium cylinder under helium atmosphere and sealed with indium wire. The cylinder was then introduced into a cryofurnace whose contribution to the neutron-count background was minimized by means of an oscillating radial collimator. All the patterns were refined by using the Rietveld refinement FULLPROF suite [12].

## III. RESULTS AND DISCUSSION

### A. Magnetization measurements

The inverse magnetic susceptibility  $1/\chi(T)$  measured at 5 mT (see Fig. 2) indicates an effective magnetic moment,  $\mu_{\text{eff}} = 0.5(1)\mu_B$ . Its value, far smaller than the corresponding Cu single-ion spin-only magnetic moment ( $1.73\mu_B$ ), suggests

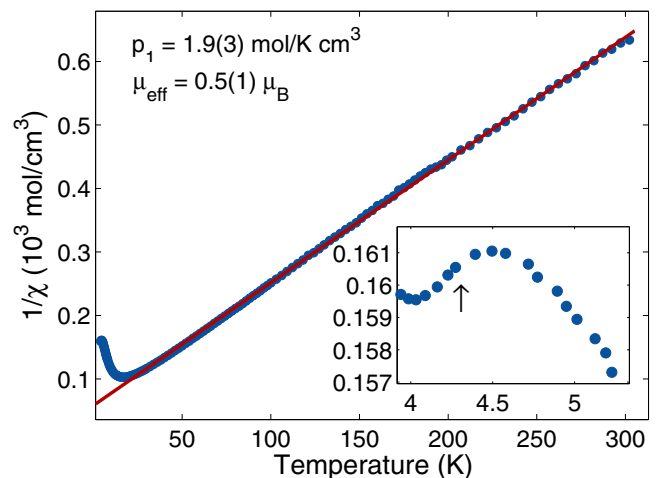


FIG. 2.  $1/\chi(T)$ , as measured at 5 mT. The linear fit (red line) to the data in the paramagnetic regime ( $T > 20$  K) implies an effective magnetic moment of  $0.5(1)\mu_B$ , while the negative intercept on the  $T$  axis indicates AFM interactions among the  $\text{Cu}^{2+}$  ions. Inset: Low-temperature  $1/\chi(T)$  data. The arrow at  $T_N = 4.24$  K indicates the inflection point, considered as the onset of AFM order [6].

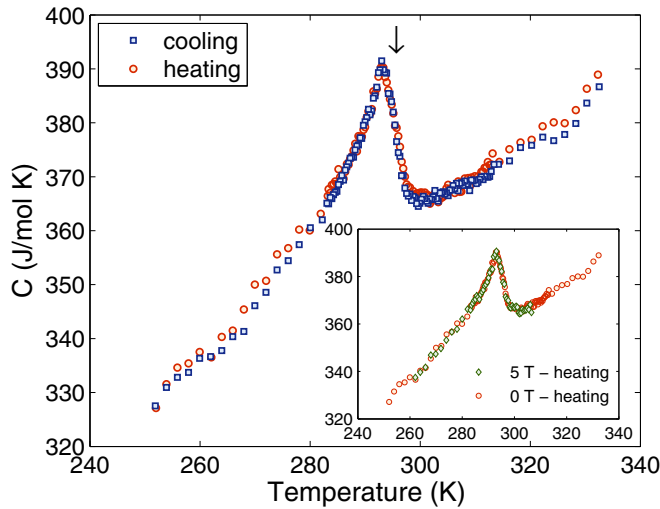


FIG. 3. The temperature dependence of the heat capacity measured upon heating and cooling shows the lack of hysteresis. The arrow indicates  $T^* = 294$  K. Inset: The coinciding 0- and 5-T data sets rule out heat-capacity changes in the applied magnetic field range.

the presence of strong quantum fluctuations. As previously reported [4], an enhancement of  $\mu_{\text{eff}}$  in higher magnetic fields may be interpreted as a field-induced suppression of the quantum fluctuations. Besides the clear anomaly at  $T_N \sim 4.2$  K, the  $\chi_m(T)$  response remains paramagnetic up to 300 K, thus excluding the magnetic nature of the transition observed at  $T^* = 294$  K (see below).

### B. Specific-heat measurements

The heat capacity data vs temperature, collected between 250 and 330 K upon both heating and cooling, are shown in Fig. 3. The significant and overlapping (i.e., hysteresis-free) anomalies both peak at 293 K and indicate the existence of a previously unnoticed second-order phase transition in this temperature range. The independence of the transition from the applied magnetic field (of 5 T in this case, see inset in Fig. 3) and the absence of an anomaly in the magnetic susceptibility (see Fig. 2) rule out a magnetic origin of the transition and suggest the transition at  $T^*$  to be of *structural character*. From the heat-capacity data, we calculated numerically the entropy  $\Delta S(T) = \int_{T_0}^T C_p d(\ln T)$ , with  $T_0$  being a reference temperature. Since across  $T^*$  we find  $\Delta S(T) \sim R$  ( $=8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ), this suggests an order-to-disorder (i.e., a nondisplacive) type of structural transition (see below).

### C. Nuclear magnetic resonance measurements

The  $^{35}\text{Cl}$  NMR lines measured at different temperatures are shown in Fig. 4. The formation of two magnetic sublattices in the AFM phase, below 4.24 K [6], is clearly manifested in the line splitting and broadening of the  $T = 4$  K data set. Most important to us is the line behavior in the high-temperature regime. Figure 5 shows the evolution of the peak positions [Fig. 5(a)] and of their separation [Fig. 5(b)] with temperature. Below  $T^* = 294$  K, the two distinct NMR lines correspond to two crystallographically inequivalent chlorine sites. Their

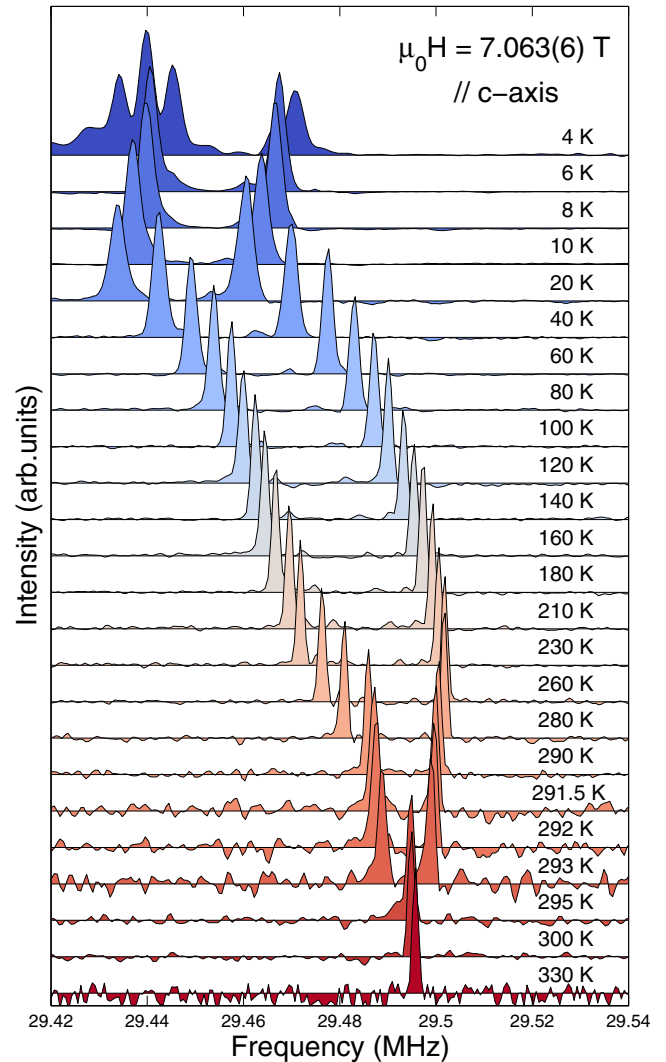


FIG. 4. Evolution of the  $^{35}\text{Cl}$  NMR line shape and position with temperature. Note that at room temperature  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  exhibits a positive paramagnetic shift of  $\sim 0.1\%$ , with respect to the Larmor frequency (29.466 MHz in a 7.063-T magnetic field). At  $T^* = 294$  K, the two NMR lines resulting from the two inequivalent chlorine sites merge into a single peak, indicating that the structural transformation of the  $\text{ClO}_4^-$  tetrahedra is complete.

merging at  $T^*$  suggests a structural transition of certain structural subunits to a higher symmetry, which reestablishes the site equivalence and preserves it upon heating up to at least 330 K. This transition is even better illustrated by the peak-to-peak distance vs temperature plot [see Fig. 5(b)]. The peak separation exhibits first a shallow maximum centered at 175 K, then it continuously decreases, to finally vanish at  $T^* = 294$  K, a value very close to that of the maximum in the heat-capacity  $C(T)$  data (293 K).

Note that both the Knight shift and the static susceptibility [6] (i.e., the magnetization data) exhibit a very similar temperature dependence. In particular, the susceptibility data were compared to those calculated by quantum Monte Carlo simulations and, upon assuming the validity of a 2D Heisenberg model on a square lattice (see Fig. 3 in Ref. [6]), an excellent agreement was found.

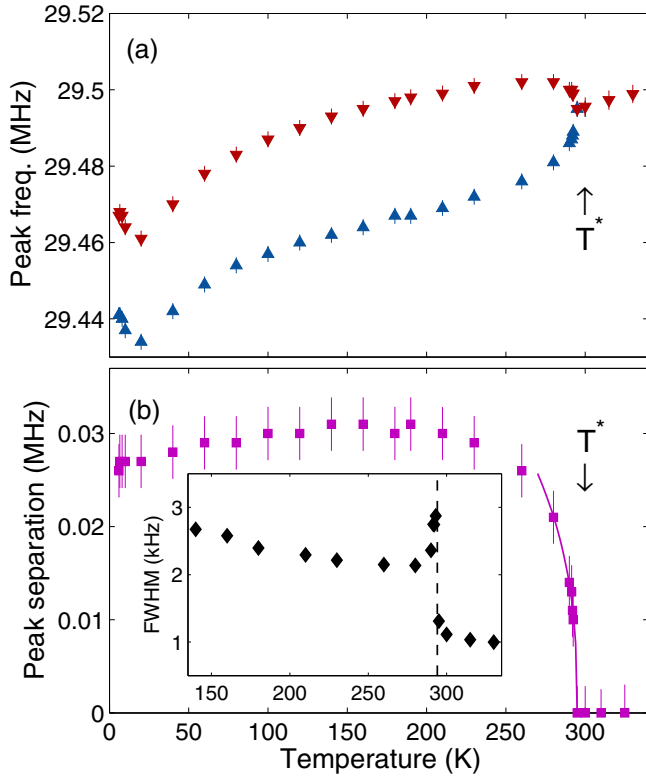


FIG. 5. (a)  $^{35}\text{Cl}$  NMR peak positions vs temperature. Despite a general increase in frequency with temperature, the peak separation (b) stays mostly constant ( $\sim 30$  kHz), to smoothly go to zero at  $T^* = 294$  K (see arrows). The line is a fit to  $(1 - T/T^*)^\beta$ , with  $\beta = 0.45(5)$ . Inset: Upon heating, the NMR linewidth shows a clear drop at  $T^*$  (dashed line), indicative of a transition to a configuration with higher local symmetry.

By relating the frequency shifts  $K_s(T)$  of the two  $^{35}\text{Cl}$  NMR lines to the susceptibility data  $\chi(T)$  at the corresponding temperatures, we obtain the so-called Clogston-Jaccarino plot [13], with  $T$  as an implicit parameter. This is shown in Fig. 6 and was used to evaluate the amplitude of the hyperfine interaction  $A_{\text{hf}}$ . In our case, this is the same for both  $^{35}\text{Cl}$  sites,  $A_{\text{hf}} = -10(5)$  mT/ $\mu_B$  (see parallel fit lines in Fig. 6), and was calculated by means of [14]

$$K_s = gA_{\text{hf}}\chi + K_{\text{orb}}, \quad (1)$$

by assuming a standard electronic  $g$  factor of 2.0. By extrapolating the straight line fits to  $\chi_m = 0$  (see Fig. 6), we obtain an orbital (i.e., temperature-independent) shift  $K_{\text{orb}}$  of 0.13% for the upper line and of 0.03% for the lower one. Above  $T^*$ , the shift of the single NMR line extrapolates to 0.108%, in excellent agreement with the typical values of  $^{35}\text{Cl}$  chemical shift in the perchlorates (e.g., 0.105% in  $\text{KClO}_4$ ) [15]. While the latter reflects the undistorted geometry of the  $\text{ClO}_4^-$  tetrahedra, the rather different  $K_{\text{orb}}$  values observed below  $T^*$ , differing by approximately +25% and -75%, respectively, are strong indicators of a significant deviation from the structural configuration adopted above  $T^*$ . Considering that the  $^{35}\text{Cl}$  nuclei are located inside the tetrahedra, the change of  $K_{\text{orb}}$  across  $T^*$  has to be related to a static or dynamic modification of the

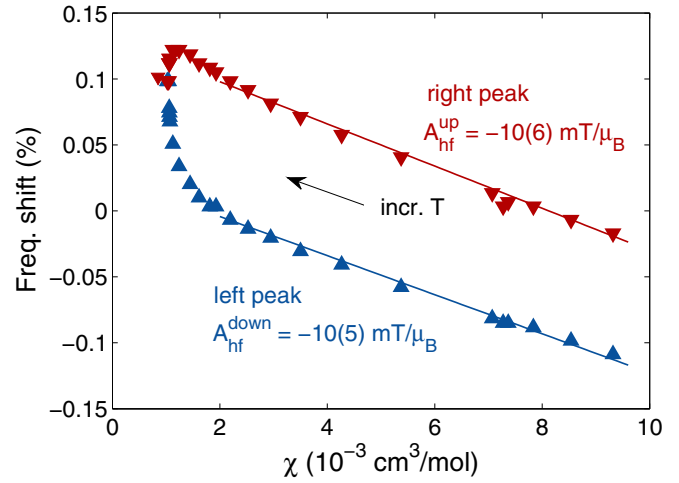


FIG. 6. The Clogston-Jaccarino  $K_s(T)$  vs  $\chi(T)$  plot for the two inequivalent chlorine sites. The almost identical slopes result in the same hyperfine coupling value,  $A_{\text{hf}} = -10(5)$  mT/ $\mu_B$ . The purely linear behavior is modified when the NMR signals start to merge. The arrow indicates the direction of increasing temperature.

tetrahedra, as confirmed by neutron-diffraction experiments (see below).

Since the NMR spin-lattice relaxation rates  $1/T_1$  are known to be very sensitive to phase transitions [16,17], we performed detailed  $T_1$  measurements in the temperature range between 280 and 320 K. The relaxation-rate data collected by means of the inversion-recovery method (see Fig. 7) confirm the presence of an anomaly at 295(1) K, compatible with the  $T^*$  value, here defined as the merging point of the two distinct  $^{35}\text{Cl}$  NMR lines. The  $T_1$  values were determined from fits using the formula relevant for spin-3/2 nuclei [18]:

$$M_z(t) = M_0[1 - f(0.9e^{-(6t/T_1)^\lambda} + 0.1e^{-(t/T_1)^\lambda})]. \quad (2)$$

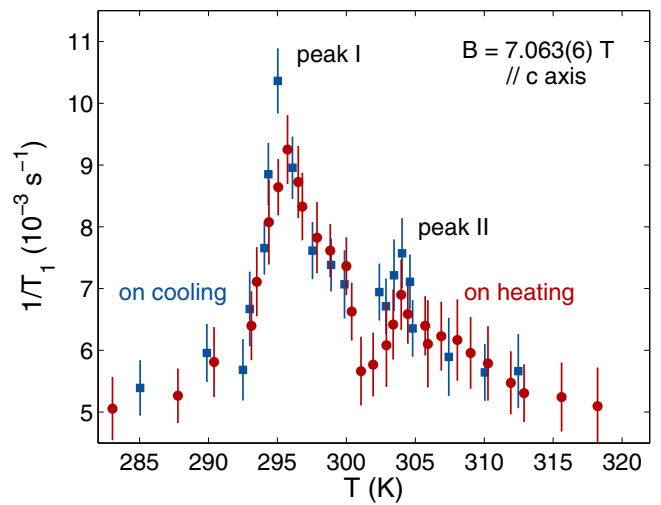


FIG. 7.  $^{35}\text{Cl}$  NMR spin-lattice relaxation rate  $1/T_1$  vs temperature measured upon heating (red circles) and cooling (blue squares). Both data sets exhibit a main peak (I) at 295 K and a smaller secondary peak (II) at 304 K. To compensate for a known calibration offset, data measured upon heating were shifted by  $-2.0$  K.



Here  $M_0$  is the saturation value of nuclear magnetization, the parameter  $f$  is ideally 2 for a full inversion, while  $\lambda$  ( $\leq 1$ ) is a stretching coefficient which accounts for a possible distribution of spin-lattice relaxation times around the mean  $T_1$  value. In our case, we find  $f \sim 1.6(2)$  and  $\lambda \sim 0.82(9)$  in the entire investigated temperature range. Both parameters exhibit a smooth variation across  $T^*$ , once more suggesting the structural character of the transition. Since the two  $^{35}\text{Cl}$  NMR lines show very similar  $T_1$  values, in the following we refer to only one of them, i.e., to the low-frequency signal.

The two data sets shown in Fig. 7 correspond to the relaxation rates  $1/T_1$  measured upon cooling (blue) and heating (red). In both cases a clear peak is observed at 295 K, with a small yet distinct anomaly peaking at  $T^{**} = 304$  K. The latter most likely reflects a minor change in the local atomic configuration, as suggested by neutron-diffraction data (see below). The lack of hysteresis, confirmed also by the previously mentioned heat-capacity data, is indicative of a second-order phase transition. In the covered temperature range (up to 320 K), no other peaks or anomalies were detected. Earlier NMR studies of pure pyrazine [19,20] reported two anomalies at similar temperatures (301.5 and 309 K, respectively), which were interpreted as partial order-to-disorder transitions.

This similarity poses the question of whether this structural transition is also featured in other molecular-copper complexes containing stacked pyrazine rings, such as the one-dimensional chains in  $\text{Cu}(\text{pz})(\text{NO}_3)_2$  [21] or the two-dimensional  $\text{Cu}(\text{pz})_2\text{X}_2$  family [2] (here  $X$  indicates a counterion, e.g.,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$ ). The role of counterions and ligands in  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  was previously investigated by DFT calculations [8]. These indicate that relevant structural changes with static or dynamic character may occur in  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  and consist of shearinglike distortions of the pyrazine rings [8], in hydrogen-bonding effects [22], or in the reorientation, deformation, and freezing of the perchlorate counteranions [8]. The latter work reported a positive correlation between the intensity of AFM exchange interactions and the shearinglike distortions of pyrazine rings, suggesting that this may also be observed in other  $\text{Cu}(\text{pz})$ -based magnets. Furthermore, if the distribution of counterions is neglected, even tiny differences in the interatomic distances in the  $\text{Cu}-\text{N} \cdots \text{N}-\text{Cu}$  magnetic pathways give rise to sizable differences in the intensity of in-plane exchange interactions, regardless of the canting angle of the pyrazine ligands. Theoretical calculations considered also different types of counterions and concluded that the spin density on the central pyrazine and, hence, the magnetic exchange interaction are enhanced by the more electronegative external atoms, as is the case of  $\text{ClO}_4^-$ . To assess whether, in our case, the detected phase transitions are due to one or more of the above-mentioned changes predicted by DFT calculations, we had to perform neutron-diffraction experiments.

#### D. Neutron diffraction

The magnetization, specific-heat, and NMR results shown in the previous sections suggest a structural origin for the two transitions at  $T^* = 294$  K and  $T^{**} = 304$  K. To closely monitor the evolution of the crystal structure between 260 and 330 K we performed systematic neutron powder-diffraction

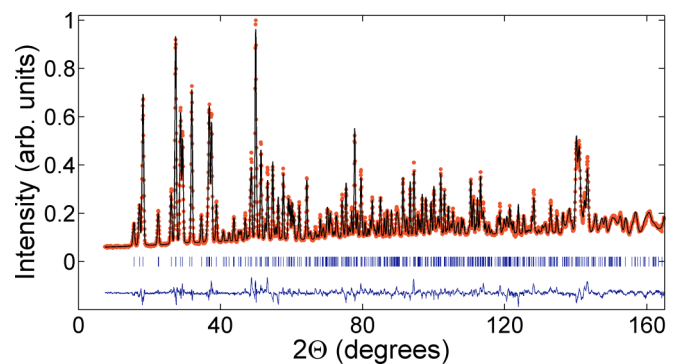


FIG. 8. A typical neutron-diffraction pattern measured at 294 K using  $\lambda = 1.8857$  Å. Circles correspond to the observed pattern and the black solid line to the Rietveld fit obtained using the  $C2/m$  space group. The positions of the Bragg reflections and the difference between the observed and calculated patterns are shown in blue.

measurements. The initial structure refinement at 295 K, i.e., just above the transition, was carried out by assuming as valid the  $C2/m$  space group, previously proposed in the literature for the structure at 293 K [1]. A representative Rietveld fit is shown in Fig. 8.

The systematic extinctions when using this space group were found compatible with the high-resolution synchrotron x-ray powder-diffraction data collected above and below the transition (260 and 295 K), and refined by using the Le Bail method [23]. Besides  $C2/m$ , we also tried its subgroups  $C2$  and  $Cm$ , indistinguishable in terms of solely systematic extinctions, but providing additional degrees of freedom (see Table I). The three groups were also tested with neutron data recorded at 260 and 295 K. Rietveld refinements using the  $C2$  group, for which the absence of a mirror plane implies 4/4/2 different C/D/N Wyckoff positions (instead of 2/2/1 in the  $C2/m$  case), provided slightly more realistic results for the environment of Cl in the perchlorate groups and better reliability indexes. However, the larger number of free parameters resulted in the appearance of correlations and less stable fits.  $C2/m$ , which imposes additional restrictions, resulted in an improved fit stability and fewer correlations. Hence  $C2/m$  was finally preferred for the description of the crystal structure across the full 260–330 K temperature range. The obtained values of the atomic coordinates and Debye-Waller factors (see Figs. 9 and 12), and in particular those of two of the oxygens in the perchlorate groups, should be considered with caution as they represent averages of the

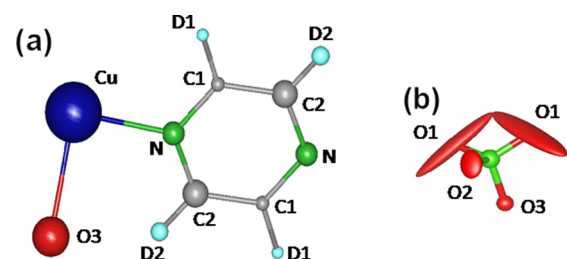


FIG. 9. (a) Structural fragment of the pyrazine ring with labels identifying each atom. (b) Thermal ellipsoids of oxygen atoms in the  $\text{ClO}_4^-$  perchlorate anions at 294 K. Note the large displacements of the two O1 atoms.

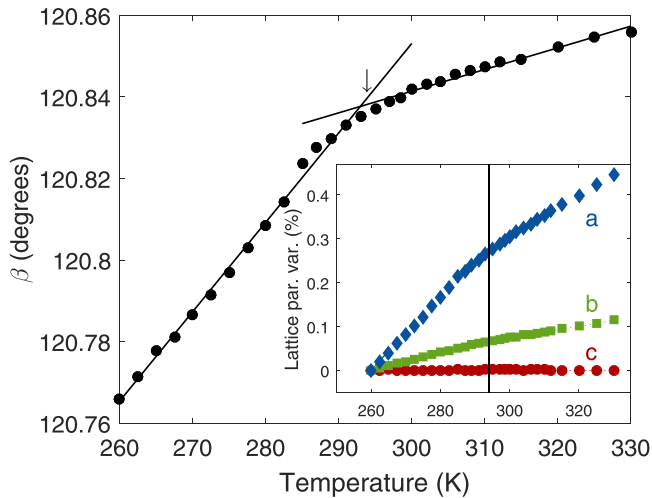


FIG. 10. Relative variation of the lattice parameters  $a$ ,  $b$ , and  $c$  (inset) and of the monoclinic angle  $\beta$  (main panel) with temperature. The interlayer axis ( $c$ ) is almost constant, and the  $b$  axis increases smoothly, whereas the  $a$  axis exhibits a tiny kink close to  $T^*$  (vertical line). The monoclinic angle  $\beta(T)$ , too, shows a clear change of slope across the transition (arrow).

atomic positions in the actual (disordered) crystal structure. The resulting structural parameters and the agreement factors obtained at 295 K with the two space groups are reported in Table I (see the Appendix).

Figure 10 shows the temperature evolution of the four lattice parameters ( $a$ ,  $b$ ,  $c$ , and the monoclinic angle  $\beta$ ), as obtained from fits based on the  $C2/m$  space group. While  $\beta$  exhibits a clear change in slope at  $T^*$ , no evident features close to the transition temperature were observed in the remaining lattice parameters, except for a tiny change in slope of  $a(T)$  close to  $T^*$ . From the NMR data, modifications related to the static (or dynamic) configuration of the perchlorate tetrahedra are expected. The above anomalies in the lattice parameters may also reflect the atomic rearrangements within the unit cell.

In spite of the above-mentioned restrictions, the structural parameters obtained from fits based on the  $C2/m$  space group provide information not only on the atomic rearrangements, but also on the average structural disorder through the analysis of the Debye-Waller factors. The latter quantify the mean-square displacements  $U_{ij}$  (ADP, i.e., atomic displacement parameter) of each atom from its average position. In harmonic crystals,  $U_{ij}$ 's can be interpreted in terms of time-averaged mean-square displacements resulting from the normal modes of vibration. In disordered materials, however, they can also capture displacements due to positional disorder [24–27]. The  $\beta_{ij}$  values, defined as  $\beta_{ij} = 8\pi^2 U_{ij} x_i^* x_j^* / 4$ , with  $x_i^*$  and  $x_j^*$  the reciprocal-cell parameters, were obtained from Rietveld fits with the FULLPROF suite package [12].

As shown in Fig. 9(b), the thermal ellipsoids described by the ADPs are remarkably large for two of the three oxygen atoms that are not bound to a Cu magnetic site [here bound to O3; see Fig. 9(a)]. The two oxygen atoms labeled O1 exhibit the largest displacements, and their  $\beta_{22}$ ,  $\beta_{33}$ , and  $\beta_{23}$  ADPs show clear anomalies across  $T^*$  (see Fig. 11). From 260 to 290 K the diagonal terms  $\beta_{22}$  and  $\beta_{33}$  clearly decrease,

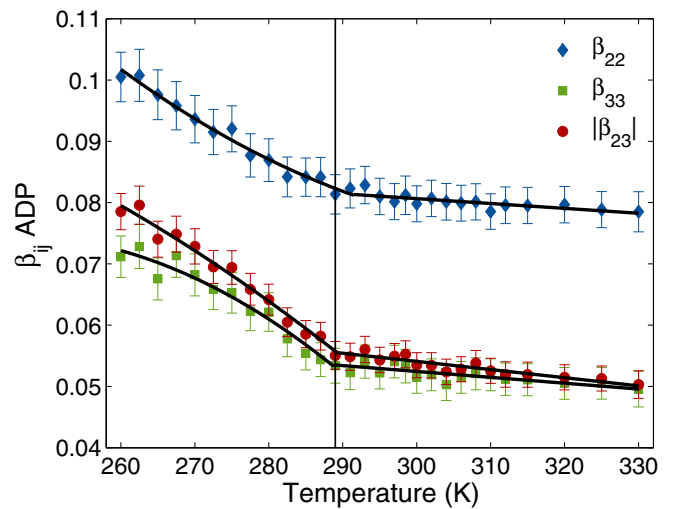


FIG. 11. Temperature dependence of the diagonal  $\beta_{22}$  (blue diamonds) and  $\beta_{33}$  (green squares) O1 ADPs and of the absolute value of the off-diagonal  $\beta_{23}$  term (red circles). The crossing of the parabolic and linear fits (black solid lines) was used to better define the position of the anomaly at  $\sim 290$  K (vertical line).

to become almost constant above  $T^*$ . The same reduction (in absolute value) is observed in the negative off-diagonal term  $\beta_{23}$ , which also saturates above 290 K. Such general reductions of the absolute ADP values indicate a decrease of disorder above  $T^*$ . The decrease of local disorder within the tetrahedra upon heating seems at first counterintuitive. Yet, it is in line with NMR results, which also indicate the number of inequivalent Cl sites (inside the  $\text{ClO}_4^{4-}$  tetrahedra) to decrease upon heating from two to one at  $T^*$ . A possible explanation for the enhanced degree of disorder at lower temperatures might be given by the coexistence of two competing oxygen positions. Note that significantly large ADP values persist also above  $T^*$ , most likely indicating the presence of a residual positional disorder.

As shown in Fig. 12, the transition at  $T^*$  also involves subtle structural anomalies related to a distortion and reorientation of the four pyrazine rings. For instance, the N-D1 distance first increases up to 288 K and then saturates, whereas the  $y$  and  $z$  atomic coordinates of the N atoms first rapidly decrease down to  $T^*$  and then continue decreasing with a reduced rate or saturate, respectively. We recall that  $x$ ,  $y$ , and  $z$  are the atomic coordinates, referring to the basis vectors  $a$ ,  $b$ , and  $c$ , respectively. As for the  $x$  coordinate, it increases linearly across the covered temperature range, without showing any evident anomalies. Incidentally, the crossing of the  $x$ - and  $y$ -coordinate values at about 308 K suggests a more regular in-plane arrangement of the pyrazine ligands above the second, yet much weaker, transition at  $T^{**}$ . This corresponds to the pyrazine rings becoming closer to regular undeformed hexagons. We note also that the rings are not perfectly flat. Nevertheless, considering the small deviations from an ideal plane, we still can define a dihedral angle  $\theta_d$  between the average plane of the pyrazine rings and the basal plane of the Cu tetrahedra. The temperature dependence of the dihedral angle is shown in Fig. 12(a) (right scale). This angle, very close to the values reported in the literature [10], decreases

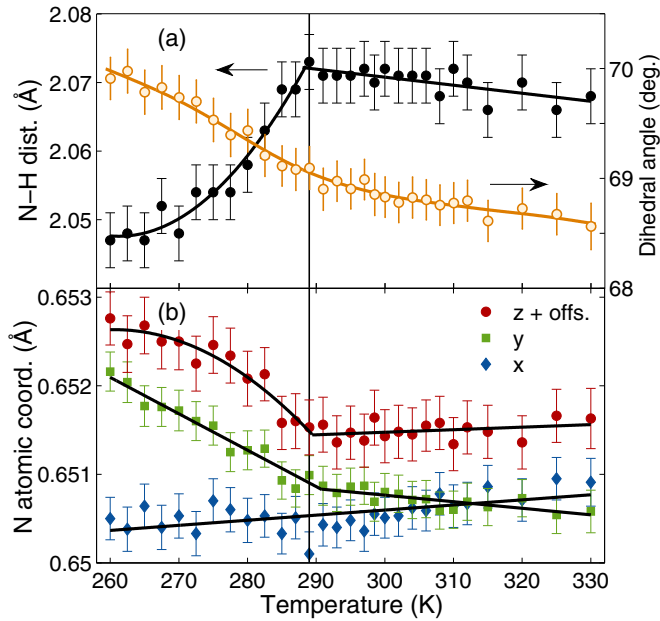


FIG. 12. Temperature dependence of (a) the N-D1 distance and of (b) the atomic coordinates of the N atoms. In all cases, the crossing of parabolic (linear) and linear fits (black solid lines) was used to define the position of the anomaly at  $\sim 290$  K (vertical line). In (b), the  $x$  and  $y$  coordinates cross at about 308 K. For clarity, the  $z$  values were vertically offset by 0.647 Å. The dihedral angle, also shown in (a), decreases with temperature and exhibits an inflection point at  $\sim 290$  K.

with temperature. Albeit weakly, the structural transition at  $\sim 290$  K is here reflected in an inflection point in  $\theta_d(T)$ .

In any case, such modifications are subtle and modest in magnitude. We also note that the small mismatch between the transition temperature  $T^*$ , established as outlined in Secs. III B and III C, and the anomalies in the neutron-diffraction data are most likely due to temperature control and calibration issues, which are difficult to control exactly in experiments at room temperature. Moreover, we recall that the Cu-N and Cu-O3 distances do not exhibit clear anomalies at  $T^*$  and that the ratio  $d(\text{Cu-N})/d(\text{Cu-O3})$ , reflecting the degree of the Jahn-Teller distortion of the octahedra centered at Cu sites, has a constant value of  $1.14 \pm 0.08$ . Finally, both the in-plane N-Cu-N and the apical O-Cu-N angles are close to  $90^\circ$  and tend to the exact value of  $90^\circ$  upon increasing temperature. The absence of significant changes in these angles, which control the overlap of the CuN and CuO orbitals, indicates that the phase transition reported here does not imply sizable changes in the strength of the superexchange interactions.

To provide a possible explanation for the above observations, we recall that structural phase transitions can be classified as either displacive or order-disorder type, usually considered mutually exclusive. The latter consists in the transition from a configuration where one or more sites exhibit split occupancies to a more ordered one within the same set of atomic positions. From our neutron-diffraction and  $C_p(T)$  measurements, we conclude that the observed transition is a

second-order structural transition of the order-disorder type (with some possible residual displacive effects). In fact, below  $T^*$ , two locally different Cl sites can be distinguished and, hence, the system is disordered. Above  $T^*$ , despite the established equivalence of the two Cl sites, some residual disorder persists, most likely due to the coexistence of two similar configurations of the perchlorate subunits.

#### IV. CONCLUSION

By combining the results of magnetization, specific-heat, NMR, and neutron-diffraction experiments, we identified a previously unnoticed second-order phase transition at  $T^* = 294$  K in  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  and determined its order-to-disorder structural character.  $^{35}\text{Cl}$  NMR measurements indicate the presence of two inequivalent  $^{35}\text{Cl}$  sites which persists, upon heating, up to the transition temperature. Interestingly, the distance in frequency between the two  $^{35}\text{Cl}$  NMR lines starts reducing from 175 K, i.e., the temperature at which a softening of the vibrational modes related to the pyrazine rings was previously observed. Above  $T^*$ , the measured NMR orbital shift is compatible with typical values of the  $^{35}\text{Cl}$  nucleus in a tetrahedral environment. Below  $T^*$ , instead, it assumes two significantly different values, with opposite signs for the two distinct sites, thus revealing strong deviations from the ideal tetrahedral geometry. The spin-lattice relaxation-rate data allowed us to precisely identify  $T^*$  and to observe also a minor anomaly at  $T^{**} = 304$  K, attributable to secondary structural distortions. The refinement of the neutron-diffraction patterns, assuming the validity of the  $C2/m$  space group, was used to monitor the temperature dependence of all the structural parameters. A detailed analysis indicates that the reported transition affects the perchlorate  $\text{ClO}_4^-$  tetrahedra, which adopt a more regular and ordered arrangement above  $T^*$ . The relatively high values of the atomic displacements indicate the persistence of some positional disorder also above the transition, most likely due to the competition between two possible oxygen-site positions, almost degenerate in energy. Similarly, reorientations of the pyrazine rings, occurring at the transition, are reflected in anomalies in the N-H distance and in the nitrogen atomic coordinates. As shown by magnetization and specific-heat data, these subtle structural modifications do not affect the magnetic properties of  $\text{Cu}(\text{pz})_2(\text{ClO}_4)_2$  in the covered temperature range. Future DFT calculations, which account for positional disorder and geometric distortions, are expected to provide further insight into the significance of the structural phase transition reported here.

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**APPENDIX: STRUCTURAL REFINEMENT COMPARISON BETWEEN THE  $C2/m$  AND  $C2$  SPACE GROUPS AT 295 K**

TABLE I. Structural parameters as determined from neutron powder diffraction at  $T = 295$  K, using the space groups  $C2/m$  and  $C2$ , respectively.<sup>a</sup> For the last group, that is noncentrosymmetric, the origin is floating. For that reason the  $y$  coordinate of Cu has been fixed to zero, matching the Cu position in  $C2/m$ . To further facilitate comparisons, the setting for the monoclinic cell was chosen to be the same as in [10]. For every space group the fits were carried out using a single structural model to refine simultaneously the data recorded at  $\lambda = 1.494$  and  $1.886$  Å. The related .cif files with the refinement parameters can be found in the Supplemental Material [28].

$T = 295$ K	$C2/m$ model	$C2$ model
$a$ (Å)	9.78047(9)	9.78070(7)
$b$ (Å)	9.77594(9)	9.77589(7)
$c$ (Å)	8.16470(9)	8.16488(7)
$\beta$ (deg)	120.8361(7)	120.8353(6)
Cu ( $2a$ )/( $2a$ )	[0, 0, 0]	[0, 0, 0]
$U_{\text{iso}}$ (Å <sup>2</sup> )	0.0118(9)	0.0126(9)
Cl ( $4i$ )/( $4c$ )	[0.2402(4), 0, 0.5391(5)]	[0.2599(4), 0.4925(16), 0.4607(5)]
$U_{\text{iso}}$ (Å <sup>2</sup> )	0.012(3)	0.0292(10)
O1 ( $8j$ )/( $4c$ )	[0.2052(9), 0.1075(9), 0.6031(11)]	[0.3071(18), 0.588(3), 0.388(3)]
$U_{11}$ (Å <sup>2</sup> )	0.057(5)	0.031(7)
$U_{22}$ (Å <sup>2</sup> )	0.393(14)	0.48(5)
$U_{33}$ (Å <sup>2</sup> )	0.128(6)	0.100(13)
$U_{12}$ (Å <sup>2</sup> )	0.061(6)	-0.051(14)
$U_{13}$ (Å <sup>2</sup> )	-0.030(4)	-0.035(7)
$U_{23}$ (Å <sup>2</sup> )	-0.195(7)	0.21(2)
$U_{\text{iso}}$ (Å <sup>2</sup> )	0.193(8)	0.20(2)
O1' (-)/( $4c$ )		[0.2713(19), 0.374(3), 0.397(3)]
$U_{11}$ (Å <sup>2</sup> )		0.061(10)
$U_{22}$ (Å <sup>2</sup> )		0.217(16)
$U_{33}$ (Å <sup>2</sup> )		0.176(18)
$U_{12}$ (Å <sup>2</sup> )		0.006(10)
$U_{13}$ (Å <sup>2</sup> )		0.012(11)
$U_{23}$ (Å <sup>2</sup> )		-0.173(14)
$U_{\text{iso}}$ (Å <sup>2</sup> )		0.151(15)
O2 ( $4i$ )/( $4c$ )	[0.4010(7), 0, 0.5868(9)]	[0.1025(6), 0.504(2), 0.4146(9)]
$U_{11}$ (Å <sup>2</sup> )		0.015(3)
$U_{22}$ (Å <sup>2</sup> )		0.069(5)
$U_{33}$ (Å <sup>2</sup> )		0.067(5)
$U_{12}$ (Å <sup>2</sup> )		0.005(6)
$U_{13}$ (Å <sup>2</sup> )		0.009(3)
$U_{23}$ (Å <sup>2</sup> )		0.003(7)
$U_{\text{iso}}$ (Å <sup>2</sup> )	0.042(4)	0.047(4)
O3 ( $4i$ )/( $4c$ )	[0.1363(7), 0, 0.3366(8)]	[0.3643(6), 0.503(2), 0.6617(8)]
$U_{\text{iso}}$ (Å <sup>2</sup> )	0.0311(13)	0.0335(13)
C1 ( $8j$ )/( $4c$ )	[0.8968(3), 0.7691(3), 0.1448(4)]	[0.8948(10) 0.2307(14) 0.1506(11)]
$U_{\text{iso}}$ (Å <sup>2</sup> )	0.0145(7)	0.0168(5) <sup>a</sup>
C2 ( $8j$ )/( $4c$ )	[0.7985(3), 0.6701(3), 0.1524(4)]	[0.2996(9) 0.8400(15) 0.1504(12)]
$U_{\text{iso}}$ (Å <sup>2</sup> )	0.0190(7)	0.0168(5) <sup>a</sup>
C3 (-)/( $4c$ )		[0.0997(10), 0.7683(14), 0.8572(11)]
$U_{\text{iso}}$ (Å <sup>2</sup> )		0.0168(5) <sup>a</sup>
C4 (-)/( $4c$ )		[0.7037(9), 0.1779(14), 0.8445(12)]
$U_{\text{iso}}$ (Å <sup>2</sup> )		0.0168(5) <sup>a</sup>
D1 ( $8j$ )/( $4c$ )	[1.0197(5), 0.7807(4), 0.2700(6)]	[0.0283(9), 0.2351(14), 0.2558(9)]



(Continued.)

$T = 295$ K	$C2/m$ model	$C2$ model
$Occ$	0.978(2) <sup>a</sup>	0.961(7) <sup>a</sup>
$U_{iso}$ ( $\text{\AA}^2$ )	0.0428(12)	0.0254(9) <sup>a</sup>
D2 (8j)/(4c)	[0.8379(5), 0.6088(4), 0.2768(5)]	[0.3453(8), 0.9067(14), 0.2672(9)]
$Occ$	0.978(2) <sup>a</sup>	0.961(7) <sup>a</sup>
$U_{iso}$ ( $\text{\AA}^2$ )	0.0372(10)	0.0254(9) <sup>a</sup>
D3 (-)/(4c)		[0.9892(8), 0.7973(14), 0.7166(10)]
$Occ$		0.961(7) <sup>a</sup>
$U_{iso}$ ( $\text{\AA}^2$ )		0.0254(9) <sup>a</sup>
D4 (-)/(4c)		[0.6732(8), 0.1254(14), 0.7153(10)]
$Occ$		0.961(7) <sup>a</sup>
$U_{iso}$ ( $\text{\AA}^2$ )		0.0254(9) <sup>a</sup>
N1 (8j)/(4c)	[0.6505(2), 0.65082(20), 0.0041(3)]	[0.8503(6), 0.1551(15), 0.9987(8)]
$U_{iso}$ ( $\text{\AA}^2$ )	0.0096(4)	0.0141(5) <sup>a</sup>
N2 (-)/(4c)		[0.1512(6), 0.8534(15), 0.0060(8)]
$U_{iso}$ ( $\text{\AA}^2$ )		0.0141(5) <sup>a</sup>
$\lambda$ ( $\text{\AA}$ )	1.494 1.886	1.494 1.886
$\chi^2$	5.18 8.54	3.27 5.06
$R_{\text{expt}}$	4.50 3.49	4.48 3.48
$R_{wp}$	10.2 10.2	8.10 7.82
$R_p$	9.37 9.14	7.53 7.25

<sup>a</sup>Quantities constrained to be identical for the same atomic species. The occupation of the D sites was found to be very close to 100%. The occupation of the remaining atomic sites was 100%.

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- [27] We recall that ADPs, which describe the anisotropic thermal motion through a symmetric rank-2 tensor, consist of six independent parameters. In the isotropic case, the off-diagonal terms clearly vanish. Most often  $U_{ij}$  are used to express ADPs, since they represent directly the mean-square atomic displacements (some values relevant to our case are reported in Table I). An alternative, closely related quantity is  $B_{ij} = 8\pi^2 U_{ij}$ . Computer programs generally output the  $\beta_{ij}$  values, defined as  $\beta_{ij} = B_{ij}x_i^*x_j^*/4$ , since these minimize computation time and can be related directly to the reciprocal-cell parameters  $x_i^*$  and  $x_j^*$ . The diagonal ADPs describe displacements along three mutually perpendicular axes of the ellipsoid and, hence, are always positive. On the other hand, since the other elements of the ADP tensor establish the orientation of the ellipsoid with respect to the crystal-lattice coordinate system, the off-diagonal elements can be either positive or negative, under the structural constraint  $\beta_{ii}\beta_{jj} > \beta_{ij}^2$ , which is confirmed from our data and is a necessary requirement for the physical validity of the refinement.
- [28] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevMaterials.3.053602> for the two structural .cif files used for refining the neutron-diffraction patterns at 295 K, by assuming as valid the space groups  $C2$  and  $C2/m$ , respectively.