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High-resolution neutron diffraction study of possible charge ordering in $Na_{0.5}CoO_2$

A. J. Williams,[1] J. P. Attfield,[1] M. L. Foo,[2] L. Viciu,[2] and R. J. Cava[2]
[1]*Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, King's Buildings, Mayfield Road, Edinburgh, EH9 3JZ, United Kingdom*
[2]*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*

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The structure of $Na_{0.5}CoO_2$, the low-temperature insulator that separates the antiferromagnetic and normal metals in the Na_xCoO_2 phase diagram, is studied by high-resolution powder neutron diffraction at temperatures between 10 and 300 K. Profile analysis confirms that it has an orthorhombic symmetry structure, space group *Pnmm*, consisting of layers of edge-sharing CoO_6 octahedra in a triangular lattice, with Na ions occupying ordered positions in the interleaving planes. The oxygen content is found to be stoichiometric within 1%, indicating that the Na concentration accurately determines the electronic doping. The Na ordering creates two distinct Co sites, in parallel chains running along one crystallographic direction. The differences in their Co-O bond distances and the derived bond valence sums, reflections of the degree of charge ordering in this phase, are very small.

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I. INTRODUCTION

Studies of Na_xCoO_2 and its hydrated phases have provided a wealth of experimental information on the magnetic and electronic behavior of conducting, planar triangular lattices, and have stimulated considerable theoretical interest. The structures of these materials consist of triangular planes of edge-sharing cobalt-oxygen octahedra, interleaved with either Na or $Na-H_2O$ layers. Characterization of the electronic phase diagram of Na_xCoO_2 (Ref. 1) has revealed that an insulating phase, $Na_{0.5}CoO_2$, is found at a sodium content between that of the superconductor $Na_{0.35}CoO_2 \cdot 1.4H_2O$ (Ref. 2) and the high-thermoelectric coefficient, metallic, magnetic phase $Na_{0.7}CoO_2$.[3,4,1] $Na_{0.5}CoO_2$ displays electronic and magnetic phase transitions at 87, 53, and 20 K.[5] The character of these phase transitions is not fully understood. Although insulating in the comparative sense, the behavior of the resistivity of $Na_{0.5}CoO_2$ is unconventional:[1] the in-plane resistivity increases weakly (from 1 mohm/cm) between 300 and 50 K, and then increases sharply, in two steps, at lower temperatures to reach only 20 mohm/cm by 4 K. Due to its importance in separating superconducting and magnetic parts of the phase diagram in this system, $Na_{0.5}CoO_2$ is the subject of detailed study (see, e.g., Refs 6–11). Based on a conventional neutron diffraction study, and analysis of electron diffraction patterns, it was proposed[5] that the insulating character of this compound was due to the formation of a charge-ordered state in the Co lattice induced by the formation of chains of Na running along one in-plane direction, breaking the hexagonal symmetry and creating two distinct types of Co sites. The quality of the diffraction data, however, was insufficient to characterize the CoO_2 lattice in detail. The current study, based on high-resolution powder neutron diffraction data, indicates that the structure is not as simply reflective of a conventional charge-ordered state as originally proposed, as the structural distinction between the two Co sites is very small. The results support arguments proposed based on NMR and other measurements[6–11] that subtle effects may be at play. The detailed structural information presented here provides the basis for a deeper understanding of the relationships between the structure and properties of this phase.

II. STRUCTURE ANALYSIS

The $Na_{0.5}CoO_2$ sample was synthesized from single-phase powder of $Na_{0.75}CoO_2$, itself prepared by heating stoichiometric quantities of Na_2CO_3 and Co_3O_4 overnight in flowing oxygen at 800 °C. That powder was then treated by immersion for five days (with stirring) in acetonitrile saturated with I_2 in sufficient excess to ensure full oxidation of the powder to $Na_{0.5}CoO_2$. The powder was then washed with acetonitrile and stored in a dry environment during all subsequent handling. Details of the synthesis have been described elsewhere.[1]

Powder neutron diffraction data were collected from the high resolution powder diffractometer (HRPD) instrument at the ISIS facility, United Kingdom. Long scans of approximately 6 h each were collected at 10 and 300 K. Shorter scans of around 1 h were collected at 30 K, 60 K, and 100 K to examine the structure between the three observed transitions in this material. Profiles from the backscattering ($2\theta = 168°$) and the $2\theta = 90°$ detector banks were simultaneously Rietveld analyzed using the General Structure Analysis System (GSAS) program.[12] A linear interpolation background with ten terms was used, and the peak shape was modeled using a convolution of Ikeda-Carpenter and pseudo-Voigt functions.

A model for the structure of $Na_{0.5}CoO_2$ has been proposed previously.[5] The model has an orthorhombic *Pnmm* symmetry superstructure of the basic hexagonal arrangement, with $a_0 = \sqrt{3}a_H$, $b_0 = 2a_H$, and $c_0 = c_H$, where a_H and c_H are the hexagonal subcell lattice parameters. The departure from hexagonal symmetry was attributed to the ordering of the Na into zigzag chains running parallel to b_o, leading to two different kinds of Co sites. This distinction of Co sites in a 1:1 ratio led to the proposal that a charge-ordered state in the Co plane is the origin of the insulating behavior of $Na_{0.5}CoO_2$. The diffraction data were not of sufficient quality, however,

TABLE I. Lattice and agreement parameters for $Na_{0.5}CoO_2$ at different temperatures.

T:	10 K	30 K	60 K	100 K	300 K
a (Å)	4.8763(1)	4.8764(1)	4.8765(1)	4.8765(1)	4.8761(1)
b (Å)	5.6278(1)	5.6274(2)	5.6276(2)	5.6276(1)	5.6281(1)
c (Å)	11.0620(1)	11.0618(2)	11.0635(2)	11.0694(1)	11.1283(1)
V (Å^3)	303.572(8)	303.55(1)	303.62(1)	303.78(1)	305.392(9)
χ^2	6.43	2.87	2.91	3.10	5.49
R_{wp} (%)	2.59	4.64	4.67	3.92	2.76
R_p (%)	3.91	7.79	7.59	6.50	4.13

to accurately characterize the cobalt oxygen lattice and confirm the charge ordering. See Table I for details.

There are two distinct types of Na site in the Na_xCoO_2 family of structures—both are trigonal prismatic, but one shares edges with adjacent CoO_6 octahedra (Na2), whilst the other shares faces (Na1). For a broad range of Na contents in Na_xCoO_2,[13–16] the Na2 site is favored; however, in $Na_{0.5}CoO_2$ it was proposed, and we have found, that the Na1 and Na2 sites are occupied in equal ratios. The highly resolved data from HRPD ($\Delta d/d = 4\times10^{-4}$ for back scattering data) allowed for an unconstrained refinement of the lattice parameters and atomic coordinates for $Na_{0.5}CoO_2$ to a stable minimum. The previously proposed model gives an excellent fit to the data at 10 K (Fig. 1) and 300 K, and no improvement was obtained with other superstructure models tested. There is no evidence in the neutron diffraction patterns for any structural distortions to lower symmetry than *Pnmm* down to 10 K. Free refinement of the fractional occupancies at the two Na sites, and at the vacant Na positions, showed that no disorder is present in the Na sublattice to an experimental uncertainty of 2%: The Na sublattice is fully ordered. Similarly, free refinement of the fractional occupancies at the oxygen sites indicated that no oxygen nonstoichiometry is present, to an uncertainty of less than 1%. This latter result indicates that in the Na_xCoO_2 system, the Na content x provides an excellent measure of the formal charge on the Co lattice, and therefore the electronic doping in Na_xCoO_2, at least at $x=0.5$, much as the Sr content allows one to count formal charge and doping in the cuprate superconductor $La_{2-x}Sr_xCuO_4$. The refined structural parameters and selected bond distances are given in Tables II and III.

III. DISCUSSION

The above results confirm that the symmetry of the previously proposed model for the structure of $Na_{0.5}CoO_2$ is correct and that no long-range structural distortions occur on cooling from 300 to 10 K. The weak superlattice observed at 80 K by electron diffraction was not observed in the neutron diffraction data. The lattice parameters show a highly anisotropic thermal expansion (Fig. 2), which is consistent with the layered nature of the structure. The averaged in-plane expansion from 10 to 300 K is $\alpha_{ab} = (ab/2)\cdot\Delta(ab)/\Delta T = 16$ ppm, whereas the corresponding value in the perpendicular direction is $\alpha_c = 2540$ ppm. Comparison of the average Co-O and Na-O distances in Table III shows that the latter decrease more on cooling from 300 to 10 K, and so the large α_c results mainly from the high thermal expansivity of the height of the NaO_2 layers. The volume expansion follows the trend in c, and there is no evidence for a significant volume anomaly between 10 and 300 K (Fig. 2). However, a possible in-plane lattice distortion is evidenced by the temperature variation of the a and b parameters. A maximum in a is observed at 60 K, although the b data are more noisy so the expected corresponding minimum is not clear. In the parent hexagonal $NaCoO_2$ structure, the in-plane hexagonal lattice parameter a_H is related to a and b in the present orthorhombic cell by $a_H = a/\sqrt{3} = b/2$. The plot of these normalized cell parameters in Fig. 2 demonstrates that the orthorhombic distortion of the CoO_2 planes increases on cooling from 300 to 60 K, but then decreases below 60 K. This suggests that the magnetic ordering and transition to a more insulating state in $Na_{0.5}CoO_2$ at 53 K (Refs. 1 and 8) may be accompanied by a small structural distortion but without lowering the lattice symmetry.

Figure 3(a) shows a single plane of CoO_6 octahedra in $Na_{0.5}CoO_2$, with Co-O bond distances shown from the 10 K

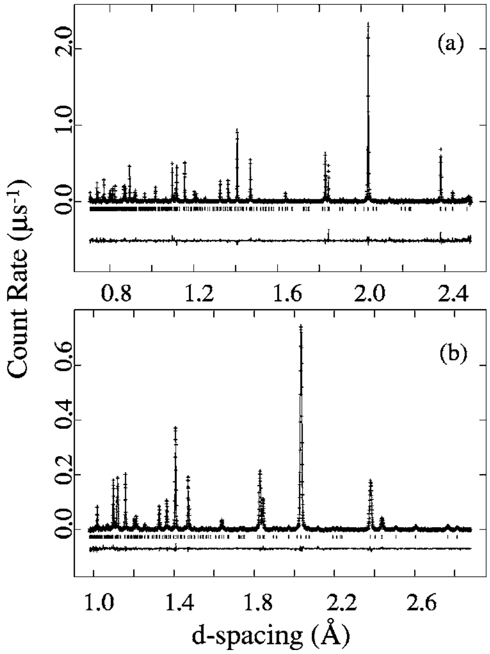

FIG. 1. Powder neutron diffraction profiles for $Na_{0.5}CoO_2$ at 10 K, fitted in orthorhombic space group *Pnmm*. (a) Backscattering ($2\theta = 168°$) and (b) $2\theta = 90°$.

TABLE II. Refined atomic parameters for $Na_{0.5}CoO_2$ at 10 and 300 K, in space group *Pnmm*.

Atom	Site	T(K)	x	y	z	U_{iso} (Å^2)
Co(1)	4*f*	10	0.0039(8)	1/4	0.0030(3)	0.0036(2)
		300	−0.0021(9)	1/4	0.0028(3)	0.0067(3)
Co(2)	4*d*	10	1/2	0	0	0.0036(2)
		300	1/2	0	0	0.0067(3)
Na(1)	2*b*	10	−0.0321(6)	1/4	3/4	0.0057(3)
		300	−0.0375(8)	1/4	3/4	0.0203(5)
Na(2)	2*a*	10	0.3609(6)	3/4	3/4	0.0057(3)
		300	0.3633(8)	3/4	3/4	0.0203(5)
O(1)	4*f*	10	0.3359(4)	1/4	0.0878(1)	0.0019(4)
		300	0.3366(6)	1/4	0.0883(2)	0.0021(5)
O(2)	4*f*	10	0.3285(4)	3/4	0.0858(1)	0.0034(5)
		300	0.3298(6)	3/4	0.0850(2)	0.0074(6)
O(3)	8*g*	10	−0.1616(4)	−0.0013(2)	0.08890(6)	0.0062(2)
		300	−0.1630(5)	−0.0020(3)	0.08843(8)	0.0093(3)

structure refinement. The chains of Co(1) and Co(2) atoms running parallel to the orthorhombic *b* axis are apparent, as is the nature in which this ordering breaks the symmetry of the ideally hexagonal CoO_2 net. The two distinct Co sites are slightly distorted from regular octahedral geometry, and do not change greatly on heating between 10 and 300 K. Co(1) shows a small off-center displacement towards one oxygen of the octahedron, while a slight tetragonal elongation (of the Co-O3 bonds) is evident in the $Co(2)O_6$ octahedron. The magnitudes of these distortions are too small for them to signify a strong, localized electron-lattice coupling, such as orbital ordering at a possible localized Co^{4+} site, in keeping with the Co charge distribution found below.

The formal cation charges at the cobalt sites are estimated by the bond valence sum (BVS) method using published parameters.[17] The values in Table III show that Co(1) has a slightly higher formal valence than Co(2). The difference at 300 K is only 7% of the ideal separation for Co^{3+} and Co^{4+} states, increasing to 12% (i.e., 3.43 vs 3.31) at 10 K. Recent studies[18–21] have shown that the structural impact of charge ordering is to lead to distinguished bond lengths (and BVS's) of 20-60% of the ideal value in symmetry-broken charge-ordered systems, where the structure has been cooled through a transition from a high-temperature structure in which all the transition metal sites are equivalent. In $Na_{0.5}CoO_2$, the symmetry equivalence of the two Co sites is

TABLE III. Structural results for $Na_{0.5}CoO_2$ at 10 and 300 K; Co-O distances (Å) and Bond Valence Sums, O-Co-O bond angles (deg.), and Na-O distances.

Type		10 K	300 K	Type		10 K	300 K
Co(1)-O(1)		1.871(4)	1.906(5)	Na(1)-O(2)	*x*2	2.321(3)	2.325(4)
Co(1)-O(2)		1.895(4)	1.873(5)	Na(1)-O(3)	*x*4	2.455(2)	2.477(2)
Co(1)-O(3)	*x*2	1.885(3)	1.880(3)	⟨Na(1)-O⟩		2.410(2)	2.426(3)
Co(1)-O(3)	*x*2	1.893(3)	1.904(3)				
⟨Co(1)-O⟩		1.887(2)	1.891(2)				
BVS [Co(1)]		3.43	3.40				
Co(2)-O(1)	*x*2	1.888(1)	1.892(1)	Na(2)-O(1)	*x*2	2.325(3)	2.319(4)
Co(2)-O(2)	*x*2	1.892(1)	1.888(2)	Na(2)-O(3)	*x*4	2.474(2)	2.489(2)
Co(2)-O(3)	*x*2	1.921(2)	1.915(2)	⟨Na(2)-O⟩		2.424(2)	2.432(3)
⟨Co(2)-O⟩		1.900(1)	1.898(1)				
BVS [Co(2)]		3.31	3.33				
O(1)-Co(1)-O(3)	*x*2	96.8(1)	96.3(2)	O(1)-Co(2)-O(2)	*x*2	96.3(1)	96.3(1)
O(1)-Co(1)-O(3)	*x*2	85.3(1)	84.3(2)	O(1)-Co(2)-O(2)	*x*2	83.7(1)	83.7(1)
O(2)-Co(1)-O(3)	*x*2	94.0(1)	94.7(2)	O(1)-Co(2)-O(3)	*x*2	95.9(1)	95.7(1)
O(2)-Co(1)-O(3)	*x*2	84.0(1)	84.7(2)	O(1)-Co(2)-O(3)	*x*2	84.1(1)	84.3(1)
O(3)-Co(1)-O(3)	*x*1	97.2(2)	97.9(2)	O(2)-Co(2)-O(3)	*x*2	96.9(1)	96.6(1)
O(3)-Co(1)-O(3)	*x*2	83.7(1)	83.9(1)	O(2)-Co(2)-O(3)	*x*2	83.1(1)	83.4(1)
O(3)-Co(1)-O(3)	*x*1	95.3(2)	94.3(2)				

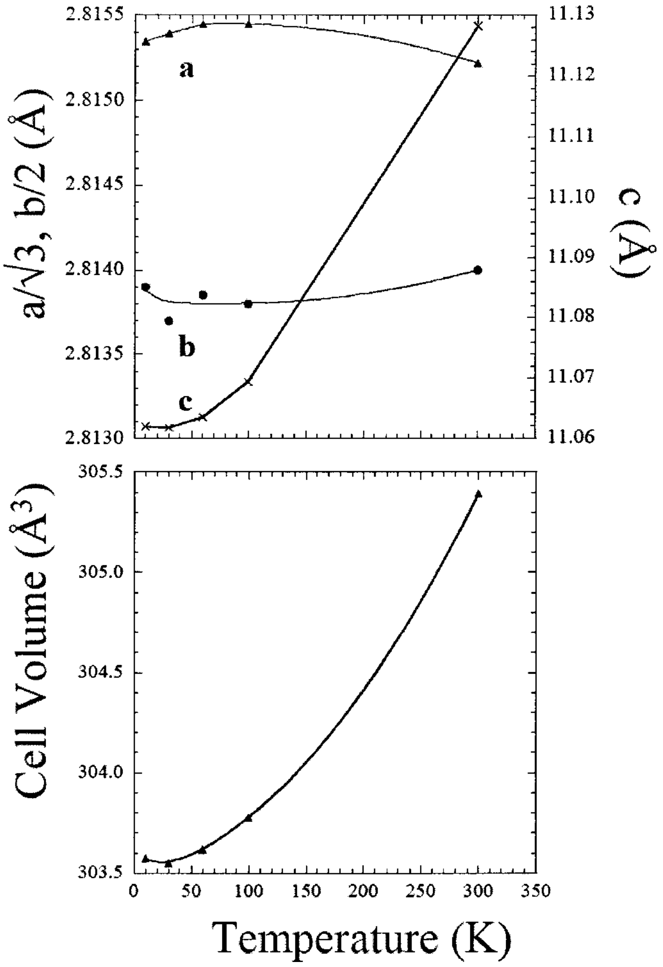

FIG. 2. Temperature dependence of (upper panel) cell parameters, shown as $a/\sqrt{3}$ (triangles), $b/2$ (circles) and c (crosses), and (lower panel) cell volume of $Na_{0.5}CoO_2$. Lines are guides to the eye. Error bars are smaller than the points.

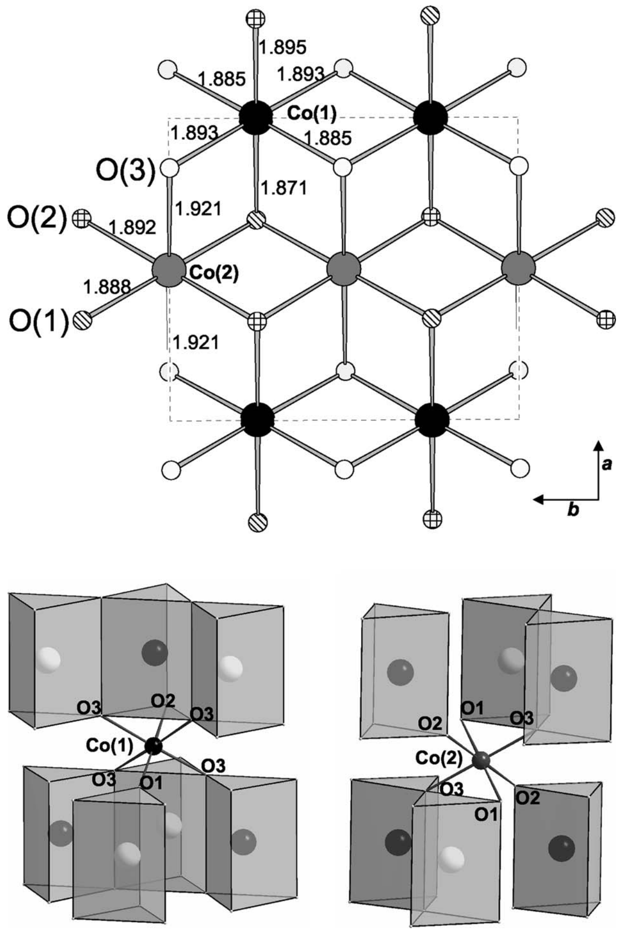

FIG. 3. (a) Detail of the structure of a single CoO_2 layer projected in the *ab* plane in the structure of $Na_{0.5}CoO_2$ at 10 K. (b) Isolated CoO_6 octahedra for the two types of Co ion [Co(1) and Co(2)]. All Na bonded to the oxygens in each CoO_6 octahedron, Na(1) in dark and Na(2) in light color respectively, are shown. The different number of near Na neighbors for each Co is illustrated. The chains of in-plane edge-sharing NaO_6 triangular prisms are also clearly seen.

broken in the orthorhombic symmetry structure by the Na ordering, and so, if the ground state was strongly insulating, the charge ordering would be expected to have a larger magnitude. In insulating Mn_2OBO_3, for example,[22] the ordering of Mn^{2+} and Mn^{3+} over two structurally inequivalent octahedral sites yields essentially 100% of the ideal bond length (or BVS) distinction. The fact that $Na_{0.5}CoO_2$ at high temperatures is only weakly nonmetallic and does not undergo a metal to insulator transition that involves a change of orders of magnitude in resistivity is consistent with our observation that the possible separation of charge on the Co(1) and Co(2) sites is far less than would be expected for a full charge-ordered state.

The original proposal for the presence of a charge ordering in $Na_{0.5}CoO_2$ was based on a local charge neutrality picture in which it was postulated that the inequivalent distributions of Na^+ ions around the Co(1) and Co(2) sites would tend to result in a lower formal charge for the Co with more near Na neighbors in accordance with Pauling's rules. The Na environments around the two Co sites, shown in Fig. 3(b) [Fig. 3(b) also clearly shows the parallel one-dimensional chains of edge-sharing NaO_6 triangular prisms that break the symmetry of the hexagonal subcell], are indeed more different than are their oxygen environments. The nearest neighbor Na^+ environments—the Na^+ ions that are bonded to the oxygens in the $Co(1)O_6$ and $Co(2)O_6$ octahedra [see Table IV and Fig. 3(b)]—involve seven sodium ions for Co(1) and six for Co(2), and there are considerable differences in the Co-Na distances in the two cases. Whether these differences in distances and local coordination number are sufficient to suggest that the original notion of "local charge neutrality" is relevant in this system is not easily resolved. However, the fact that the Co(1) site has a slightly higher formal charge than the Co(2) site (3.43 vs 3.31 at 10 K) while having more Na^+ neighbors does not support this idea.

The present structural results suggest that there is only a slight difference in electron density at the two Co sites in $Na_{0.5}CoO_2$, and that spontaneous (or Na order-assisted) full Co^{3+}/Co^{4+} charge ordering is not seen down to 10 K. Though in many cases, as described above, the manifestation of charge ordering through distortions of crystal structures is apparent,[19,20] in some cases the situation may be considered

TABLE IV. Nearest neighbor Na^+ ion distances for the Co(1) and Co(2) sites in $Na_{0.5}CoO_2$ at 10 K and 300 K. Nearest neighbor Na^+ are bonded to the oxygens in the $Co(1)O_6$ and $Co(2)O_6$ octahedra.

Type	Number	10 K	300 K
Co(1)-Na(1)	$x1$	2.805(3)	2.819(4)
Co(1)-Na(2)	$x1$	3.260(4)	3.266(5)
Co(1)-Na(1)	$x2$	3.924(2)	3.940(3)
Co(1)-Na(2)	$x1$	4.130(4)	4.155(5)
Co(1)-Na(2)	$x2$	4.334(3)	4.360(3)
Co(2)-Na(2)	$x2$	3.176(1)	3.188(1)
Co(2)-Na(1)	$x2$	3.851(2)	3.848(2)
Co(2)-Na(1)	$x2$	4.045(2)	4.073(3)

more ambiguous.[23,24] The fact that $Na_{0.5}CoO_2$ is surrounded by metallic phases at slightly higher and slightly lower electron counts in the Na_xCoO_2 phase diagram, and is only weakly insulating itself, suggests that the Co t_{2g} holes are mainly delocalized even in the $x=0.5$ phase. It may be that the Na ordering perturbs the Co-O band structure enough to open a small gap at the Fermi level, but without the substantial charge localization and ordering that occurs, e.g., in manganese oxide perovskites. Alternatively, the broken hexagonal symmetry and very small Co ion displacements within the octahedra may result in more subtle features in the electronic structure determining the properties.

It may be that underlying driving forces for a nontrivial Na-ordering scheme in $Na_{0.5}CoO_2$ cause the breaking of the hexagonal symmetry, allowing for two inequivalent Co sites to be formed that nonetheless remain very similar to each other—therefore reflecting a tendency against charge ordering. On the other hand, the opposite may be true, that is, that the symmetry breaking is driven by the tendency of the Co to charge order, and that those forces are strong enough to move the Na into a nontrivial ordering scheme. A theoretical treatment that addresses the origin of the symmetry-breaking Na-ordering array in $Na_{0.5}CoO_2$, taking into account the relative energies of the two types of Na positions, the off-center position of the Na in the site that shares edges with the CoO_6 octahedra, the Na-Na interactions, Na-Co interactions, the intrinsic tendency toward charge ordering on the Co sublattice, and the effect of such ordering on the electronic density of states, would be of great interest. Finally, more detailed study will also be of interest to determine whether the small changes in lattice parameters observed in the present study below 50 K reflect weak coupling between the electronic and magnetic transitions and structural degrees of freedom of the CoO_2 lattice in $Na_{0.5}CoO_2$ at low temperatures.

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