PHYSICAL REVIEW B **87**, 174102 (2013)

Strong magnetic-dielectric-lattice coupling in transition metal hydroxyhalides and ferroelectric response in rhombohedral $Co_2(OD)_3X$ (X = Cl, Br)

X. G. Zheng,[1,2,*] M. Fujihala,[2] S. Kitajima,[2] M. Maki,[2] K. Kato,[3] M. Takata,[3] and C. N. Xu[4,5]
[1]*Department of Physics, Graduate School of Science and Engineering, Saga University, Saga 840-8502, Japan*
[2]*Department of Physics, Faculty of Science and Engineering, Saga University, Saga 840-8502, Japan*
[3]*Structural Materials Science Laboratory, RIKEN SPring-8 Center, Kouto 1-1-1, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan*
[4]*National Institute of Advanced Industrial Science and Technology (AIST), Saga 841-0052, Japan*
[5]*International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan*

(Received 14 November 2012; revised manuscript received 25 February 2013; published 13 May 2013)

Hydroxyl salts of the type $M_2(OH)_3X$, and $M(OH)X$, where M represents a transition metal ion and X represents a halogen ion, widely exist as minerals and were recently reported to be geometrically frustrated magnets. Here, we report the finding of ferroelectric response in them. First, we observed strong magnetic-lattice-dielectric couplings in all of them as witnessed during their magnetic transitions at low temperatures. Secondly, we identified apparent ferroelectric responses in the deuterated hydroxyl salts of high crystal symmetries, i.e., rhombohedral $Co_2(OD)_3Cl$ and $Co_2(OD)_3Br$, at high temperatures of 220–230 K through an isotope effect. The present work shows that multiferroicity may be a potentially universal phenomenon in magnetic hydroxyl salts. Meanwhile, it provides the first link between magnetic geometric frustration and hydrogen-bonded soft-mode ferroelectrics.

DOI: 10.1103/PhysRevB.87.174102 PACS number(s): 77.80.−e, 61.05.cp, 75.30.−m, 77.90.+k

I. INTRODUCTION

Hydroxyl salts $M_2(OH)_3X$, and $M(OH)X$ have been known for a long time.[1,2] The most familiar might be the hydroxyl chloride $Cu_2(OH)_3Cl$ (atacamite), which forms naturally on copper and bronze as a green patina. It may also exist as a biomaterial in living organisms, where it enhances hardness and stiffness,[3,4] or as rust in electrical circuits. In recent years, the $M_2(OH)_3X$ compounds with the magnetic ions Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+} were found by us to be geometrically frustrated magnets with the magnetic ions forming triangular or tetrahedral lattices.[5–13] One well-known compound related to the hydroxyl salts is the "spin liquid" material Herbertsmithite, $ZnCu_3(OH)_6Cl_2$,[14] which is obtained by using nonmagnetic Zn^{2+} to selectively replace the magnetic ions of Cu^{2+} on the triangular-lattice planes from its parent compound clinoatacamite, $Cu_2(OH)_3Cl$.[6,7] Geometric frustration, which results from an intrinsic incompatibility between fundamental magnetic interactions and the underlying lattice geometry (triangular, tetrahedral, or kagome lattices), gives rise to intriguing fundamental phenomena such as the formation of exotic states like spin ices, spin liquids, and magnetic monopoles.[15–17] Furthermore, several mechanisms have been proposed that link geometric frustration with the origins of high-temperature superconductivity[18] and relaxor ferroelectrics. Indeed, the concept even extends to life sciences, with consequences in protein folding and neural networks.[19,20]

II. EXPERIMENTAL METHODS

The $M_2(OH)_3X$ polycrystalline samples for the present research, except the natural mineral atacamite mined from Atacamite, Chile, were synthesized using hydrothermal reactions typically from MX_2 and NaOH at temperatures ranging from room temperature to 230 °C for durations varying from several hours to one month, as reported in our previous publications. The Cu(OH)Cl compound was prepared using a different method: stoichiometric amounts of CuO and $CuCl_2\ 2H_2O$ were heated in a sealed quartz glass tube at 270 °C for one week. The dielectric measurements were performed on the two sides of a uniaxially pressed pellet specimen of the polycrystalline powders, using a precision LCR meter with frequencies ranging from 20 Hz to 100 kHz. The hysteresis measurements were carried out on an AixACCT ferroelectric test system (TFAnalyzer 2000) with an FE module. The low temperature for the measurement was obtained by using a 4-K GM cryostat. The lattice constants of the individual compounds at various temperatures were measured by x-ray diffraction at the BL44B2 beam line[21] at the RIKEN-SPring-8 synchrotron using a Debye-Scherrer camera with an imaging plate. The incident x-ray beam was monochromatized by a double-crystal monochromator tuned to a wavelength of approximately 0.5 Å for all experiments. The temperature of the sample was controlled by an Iwatani cryostat to a deviation of less than 0.2 K. Powder diffraction patterns at temperatures ranging from 300 to 3.5 K were collected over the 2θ range of 0°–68° in steps of 0.01°. The unit cell parameters were calculated and refined by the Rietveld method using the program RIETAN.[22]

III. RESULTS AND ANALYSES

A. Universal magnetic-dielectric-lattice coupling in geometrically frustrated hydroxyhalides

The magnetic hydroxyl salts, as summarized in Table I, crystallize in monoclinic, orthorhombic or rhombohedral lattices (for detailed structure and magnetism information see our previous publications[5–13]). The magnetic spins in them either form a triangle or tetrahedral lattice. Surprisingly, however, for all materials, we have observed simultaneous changes in the unit cell lengths and the dielectric constants at their respective $T_N(T_C)$s (see Table I). As exemplified in Fig. 1, the crystal lattices show changes at $T_N(T_C)$s with rapidly decreasing unit cell lengths, meanwhile, their dielectric constants also show a gradual decrease with temperature and rapid decrease below the $T_N(T_C)$s (see Fig. 2). In addition, for

TABLE I. A summary of magnetic—lattice–dielectric couplings in hydroxyl salts. For each material, at the magnetic transition temperature T_N (T_C), simultaneous changes were observed at the temperature T_ε wherein the dielectric anomaly appeared, and the temperature T_L wherein the lattice anomaly appeared. The T_N (T_C)s were determined from magnetic measurements as we previously reported in the published literature. The anomaly temperatures T_ε and T_L were determined by the present work.

Materials	Structure features	T_N (T_C)	T_ε	T_L
Atacamite $Cu_2(OH)_3Cl$	spin tetrahedra in orthorhombic lattice	$T_N \sim 9$ K (Ref. 5)	$T_\varepsilon = 8.2$ K	$T_L \sim 11$ K
Clinoatacamite $Cu_2(OH)_3Cl$	spin tetrahedra in monoclinic lattice	$T_{N1} = 18.1$ K, $T_{N2} = 6.4$ K (Refs. 6 and 7)	$T_\varepsilon = 6.4$ K	unmeasured
Botallackite $Cu_2(OH)_3Cl$	spin triangles in monoclinic lattice	$T_N = 7.2$ K (Ref. 10)	$T_\varepsilon = 7.2$ K	unmeasured
Botallackite $Cu_2(OH)_3Br$	spin triangles in monoclinic lattice	$T_N \sim 10$ K (Ref. 10)	$T_\varepsilon = 9.3$ K	unmeasured
Botallackite $Cu_2(OH)_3I$	spin triangles in monoclinic lattice	$T_N = 14$ K (Ref. 10)	$T_\varepsilon \sim 14$ K	$T_L \sim 14$ K
$R\bar{3}m$ $Co_2(OH)_3Cl$	spin tetrahedra in rhombohedral lattice	$T_C = 10.5$ K (Ref. 8)	$T_\varepsilon = 10.7$ K	$T_{L1} \sim 20$ K, $T_{L2} \sim 11$ K
$R\bar{3}m$ $Co_2(OH)_3Br$	spin tetrahedra in rhombohedral lattice	$T_{N1} = 6.2$ K; $T_{N2} = 4.8$ K (Ref. 13)	$T_{\varepsilon 1} = 6.2$ K; $T_{\varepsilon 2} = 4.8$ K	$T_{L1} = 6.5$K; $T_{L2} = 5$ K
Atacamite $Ni_2(OH)_3Cl$	spin tetrahedra in rhombohedral lattice	$T_N = 4$ K (Ref. 11)	$T_\varepsilon = 4$ K	unmeasured
Botallackite $Ni_2(OH)_3Br$	spin triangles in monoclinic lattice	$T_N = 13.5$ K (unpublished)	$T_\varepsilon = 13.5$ K	unmeasured
Cu(OH)Cl	spin triangles in monoclinic lattice	$T_N = 12$ K (unpublished)	$T_\varepsilon = 12$ K	$T_L = 12$ K

many compounds, a steep rise in the dielectric constant was observed when the temperature approached T_Ns, as demonstrated in Fig. 2. The decrease in unit cell lengths can be readily understood by closely coupled ions below $T_N(T_C)$s when the geometric frustration is relieved. However, the changes in the dielectric constants are much larger than that expected from the corresponding lattice changes. For example, in atacamite, a change of 6% in the dielectric constant was observed across the magnetic transition despite only a 0.04% change in the unit cell lengths. It is noted that the dielectric constants decreased for $T < T_N$ (T_C) while the lattice contracted. It is clear that the rapid dielectric change, in particular, the increase of the dielectric constant toward the magnetic transition, was not a consequence of lattice contraction. It has thus become clear that strong magnetic-lattice-dielectric couplings exist universally in these hydroxyl salts, thus motivating us to search for unconventional ferroelectrics like the strongly magnetic-lattice-dielectric coupled multiferroic CuO.[23,24]

B. Isotope effect and ferroelectric response in rhombohedral lattice hydroxyhalides

While it has been difficult to verify ferroelectrics at the above-mentioned low temperatures with the powder samples, we have found that for the materials $Co_2(OH)_3Cl$ and $Co_2(OH)_3Br$, which have the highest symmetry of rhombohedral lattice among the hydroxyl salts, their deuterated compounds clearly showed signatures of ferroelectricity at exceptionally high temperatures. As shown in Fig. 3(a), sharp peaks at 229 K were seen both in the real and imaginary parts of the dielectric constant for $Co_2(OD)_3Cl$, but not in $Co_2(OH)_3Cl$. In the latter, only an almost unrecognizably small change appeared at around 218 K. In addition, the dielectric constants of $Co_2(OD)_3Cl$ showed a frequency dependency resembling that of relaxor ferroelectrics [see Fig. 3(b)]. The maximum real dielectric constant clearly does not mark a phase change to a normal ferroelectric form as the maximum temperature increases with increasing measuring frequency in a manner typical for a relaxation dielectric. There is also an associated maximum in the imaginary part, again typical of the relaxor response. The quick decrease in the constant values at low frequencies is thought a result of the pressed pellet nature of the samples, which consisted of individual small grains that were loosely connected (heat treatment was not possible as it would cause dissolution of the hydroxyl salts). The electric field-polarization measurement also exhibited a hysteretic response [see Fig. 3(c)]. Similar behaviors were observed in $Co_2(OD)_3Br$ ($T_C = 224$ K at 100 kHz) but not in other deuterated compounds with lower crystal symmetries. Although spontaneous electric polarization is a stronger evidence for ferroelectric, unfortunately such measurement is not applicable for the present samples because of their powder nature. Nevertheless, the sharp dielectric response and the isotope effect agree well with a ferroelectric transition.

C. A comparative synchrotron x-ray diffraction study of $Co_2(OH)_3Cl$ and $Co_2(OD)_3Cl$

To understand the reason for the ferroelectric response, we performed a comparative synchrotron x-ray diffraction experiment for $Co_2(OH)_3Cl$ and $Co_2(OD)_3Cl$. The crystal structures at all temperatures agreed well with the room-temperature $R\bar{3}m$ structure reported by de Wolff,[25] where no off-centering of atoms existed. However, remarkable and anisotropic change in the unit cell lengths occurred upon deuteration, as seen in Fig. 4(b), with larger difference along the *a* and *b* axes

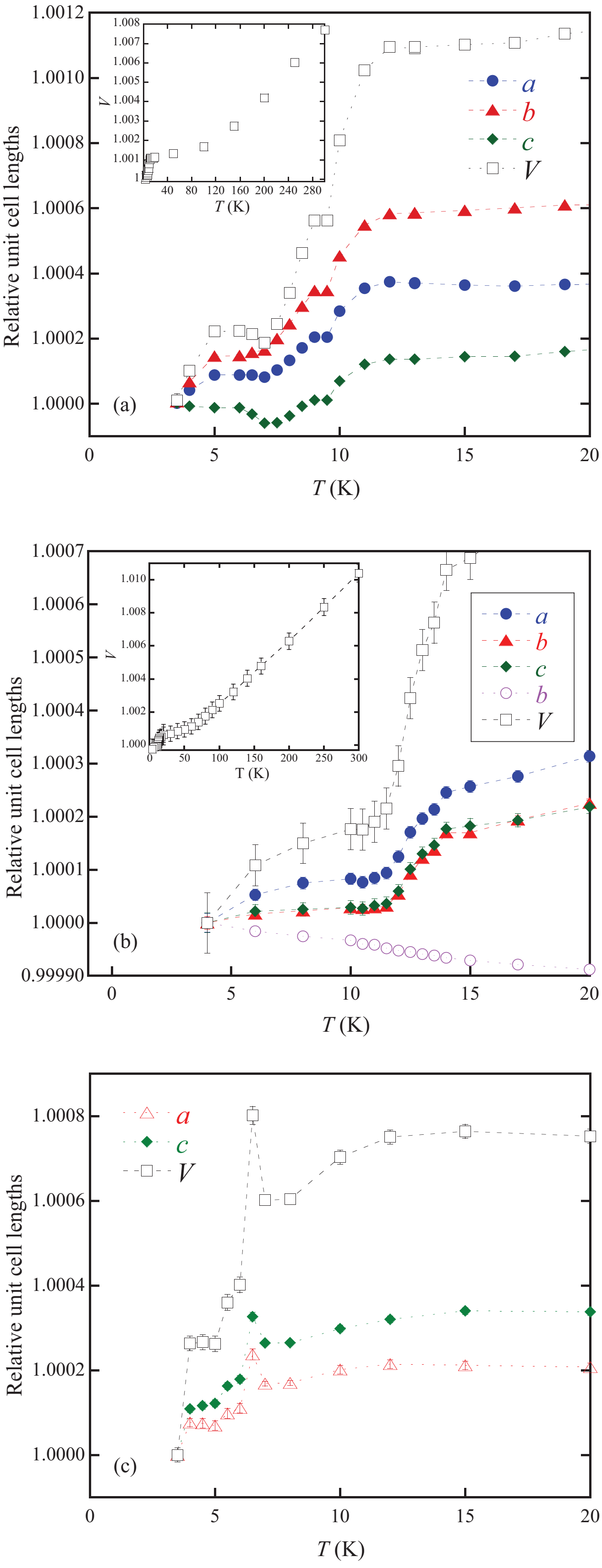

FIG. 1. (Color online) Lattice changes for representative materials of (a) atacamite $Cu_2(OH)_3Cl$, (b) $Cu(OH)Cl$, and (c) rhombohedral $Co_2(OH)_3Br$.

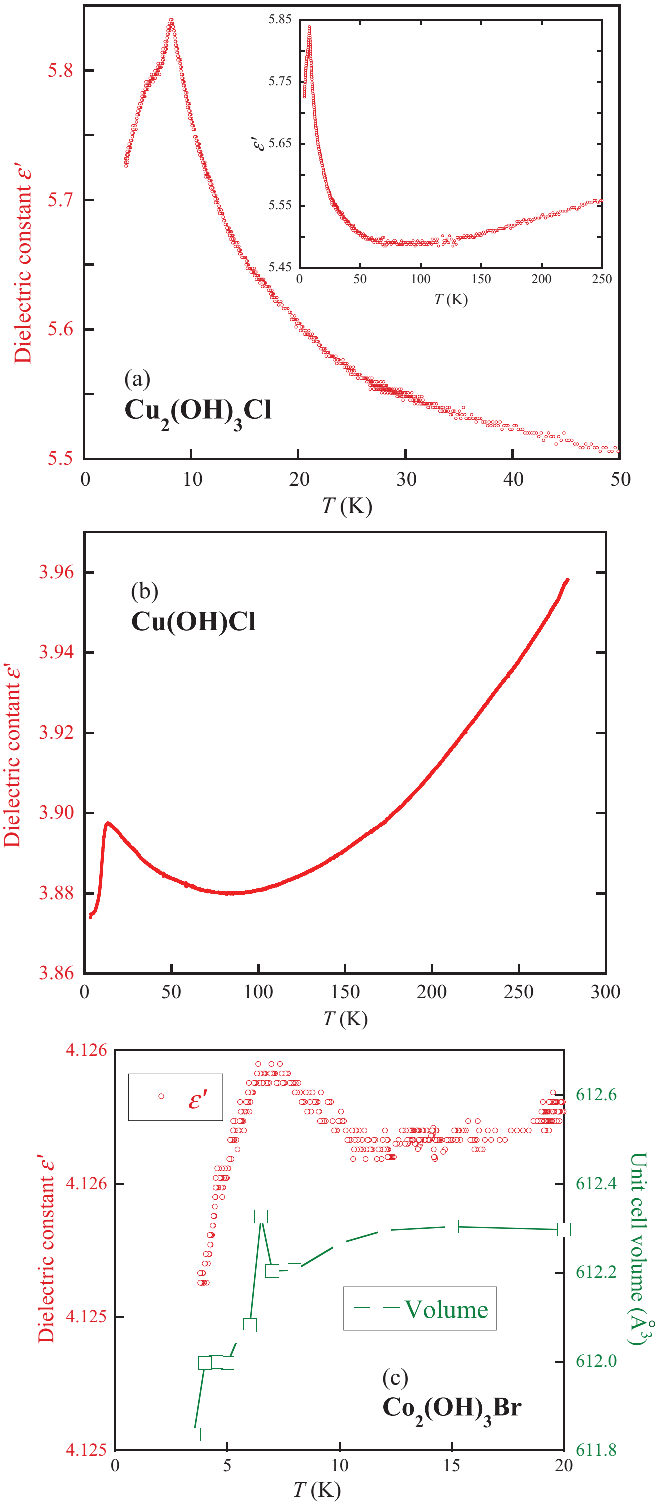

FIG. 2. (Color online) Dielectric constants measured at 100 kHz for representative materials of (a) atacamite $Cu_2(OH)_3Cl$, (b) $Cu(OH)Cl$, and (c) rhombohedral $Co_2(OH)_3Br$.

than the *c*-axis direction. More obvious changes appeared in the atomic bonding lengths with deuteration, as plotted in Fig. 4(c). We can see that the distances between the ions neighbored with nearby hydrogen, for example, the bond length between the Co ions on the kagome plane (Co1-Co1) and those between the O and Co (O-Co1 and -Co2), all

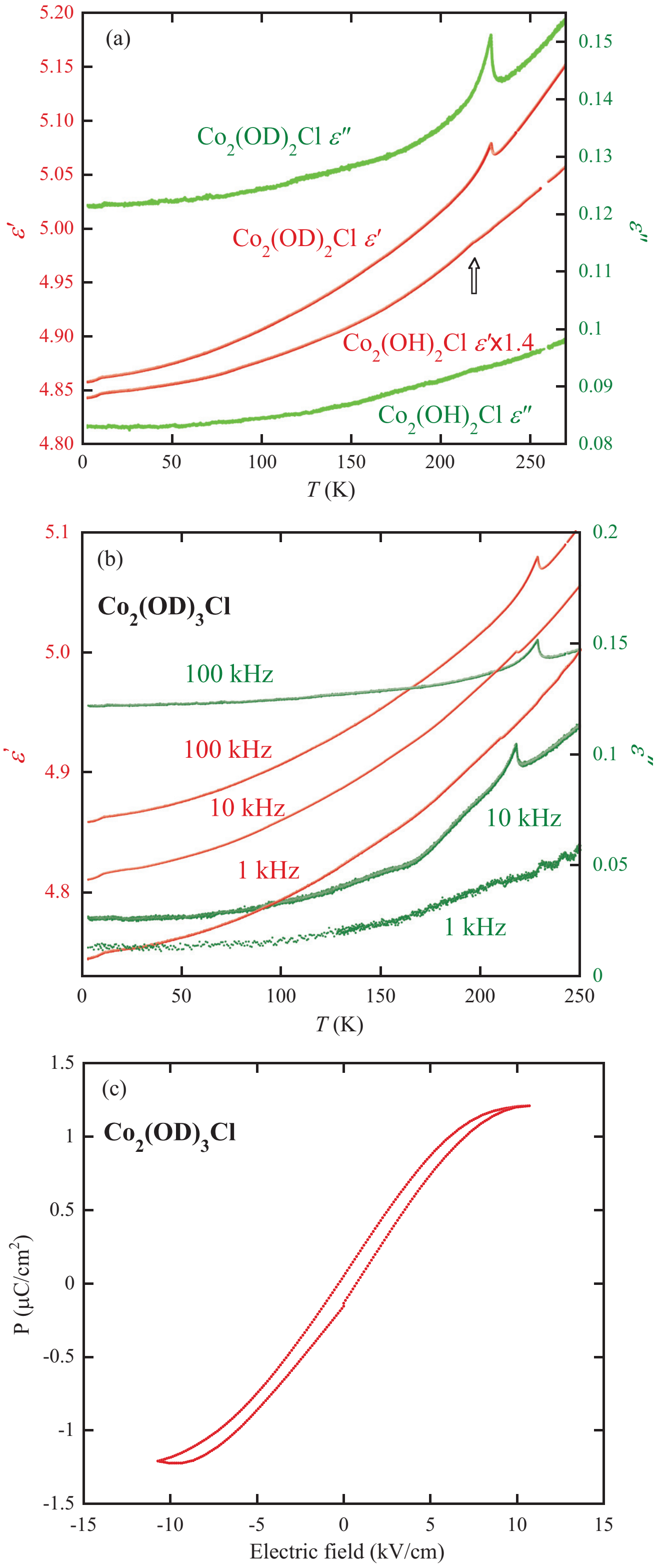

FIG. 3. (Color online) (a) Temperature dependencies of the real and imaginary parts of the dielectric constants for $Co_2(OD)_3Cl$ and $Co_2(OH)_3Cl$ at 100 kHz. The double arrow denotes a very small anomaly for $Co_2(OH)_3Cl$. (b) Temperature dependencies of the real and imaginary parts of the dielectric constants for $Co_2(OD)_3Cl$ at frequencies of 100, 10, and 1 KHz. (c) Electric field, polarization hysteresis loop for $Co_2(OD)_3Cl$ measured at 200 K and 10 kHz.

notably increased upon deuteration [refer to the structure configuration in Fig. 4(a)]. This is surprising because H and D have almost equivalent ion radii. Similar changes in the geometry of the hydrogen bonds by deuteration have long been known as the Ubbelohde effect,[26] and the quantum nature of small hydrogen atoms is believed to be the origin, although a clear picture of the quantum nuclear effects of the strength of hydrogen bonds is still unavailable.[27] There can be significant accompanying changes in the physical properties of the hydrogen-bonded materials: for example, the ferroelectric transition temperature T_C in KH_2PO_4 (KDP) increased by over 100 K on full deuteration. The small geometric changes in the hydrogen-bond dimensions were suggested to be the primary reason for the striking changes in T_C.[28] Apparently, the ferroelectricity in $Co_2(OD)_3Cl$ can be attributed to modified hydrogen bonding due to deuteration. Now we can see that the striking isotope effect exists, not only in soft materials where hydrogen bonding is the predominant bonding mechanism, but also in the present hard materials where hydrogen only plays a minor role in chemical bonding (ionic bonding of Co^{2+}-O^{2-} and Co^{2+}-Cl^- are dominating). A necessary condition for the occurrence of ferroelectricity in the hydroxyl salts $Co_2(OD)_3Cl$ and $Co_2(OD)_3Br$, we think, should be that the key ions (here the Co^{2+}) are geometrically frustrated, therefore, a very small change in the lattice and bonding breaks the balance and causes dramatic change in their physical properties.

IV. DISCUSSION AND CONCLUSION

It is interesting to note that the co-existence of ferromagnetism (antiferromagnetism) with ferroelectricity, i.e., multiferroicity, occurs in the hydroxyl salts with the highest lattice symmetry, and hence, higher geometric frustration. Strong geometric frustration in $Co_2(OD)_3Cl$ and $Co_2(OD)_3Br$ was experimentally demonstrated by the fact of low-temperature ordering despite the existence of strong magnetic couplings at high temperatures above 400 K.[8,13] The situation is in some way similar to that newly revealed for geometrically frustrated multiferroicity in hexagonal $RMnO_3$, which is a representative material for an important class of multiferroics (prime candidates for device memory applications) and is considered a prototypical multiferroic—the phenomenon can be understood as being the result of competition between local interactions at several ion sites.[29,30] The latest experimental evidence[31,32] suggests that the shifting of the positive and negative ions to induce polarization, as seen in conventional ferroelectrics such as $BaTiO_3$, is not the main driving force behind the ferroelectric transition in $RMnO_3$. Instead, the polarization is a byproduct of a very different kind of lattice distortion called a "cloverleaf" defect, that is, trimerization with a periodic lattice modulation comprising six different phases rotated through 60° with respect to each other. The threefold symmetry in rhombohedral $Co_2(OD)_3Cl$ and $Co_2(OD)_3Br$, as shown in Fig. 3(a), may play a similar crucial role as the sixfold symmetry in hexagonal $RMnO_3$. We expect future microscopic studies using a single crystal sample (though single crystals are not available at the present stage) to identify this.

Present findings also shed light on the open question of the origin of the giant isotope effect as exemplified by the

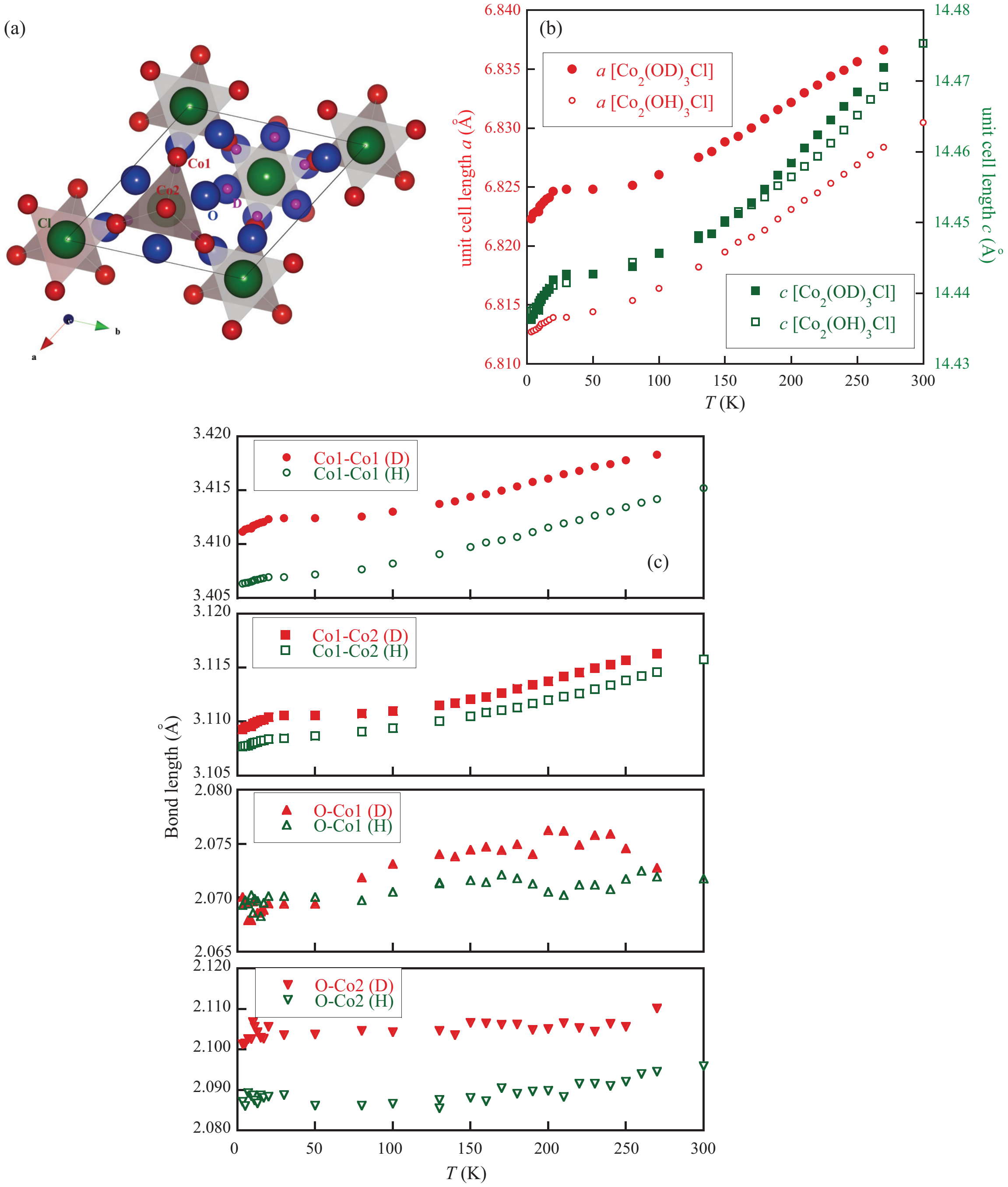

FIG. 4. (Color online) (a) Ion positions in rhombohedral $Co_2(OD)_3Cl$ projected on the *a*-*b* plane at room temperature. The position of D was determined from a neutron diffraction experiment. (b) Temperature dependencies of the unit cell parameters *a* ($a = b$) and *c* for rhombohedral $Co_2(OD)_3Cl$ and $Co_2(OH)_3Cl$. (c) Anisotropic changes in the bond lengths for rhombohedral $Co_2(OD)_3Cl$ and $Co_2(OH)_3Cl$. Due to the very small scattering of the hydrogen H(D), reliable estimation was not performed for the H(D) position.

striking increase of T_C in KH_2PO_4 (KDP) in hydrogen-bonded soft-mode ferroelectrics, which is of special interest because hydrogen bonds are essential to life on earth. Despite seven decades of considerable academic efforts, there still remains considerable controversy regarding the origin of this giant isotope effect. While it has been understood mostly in terms of the quantum tunneling of hydrogen,[33] there is strong evidence that isotope substitution acts rather through a geometrical modification of the hydrogen bonds with an expansion of the O-H-O distance.[28,34] As viewed in the crystal structure of $Co_2(OH)_3X$ in Fig. 4(a), the present hydroxyl salts do not have two equivalent sites for hydrogen tunneling, our results prove that the giant isotope effect can only be attributed to geometrical modification of the hydroxyl bonds. The combination of magnetic geometric frustration and hydrogen bonding is essential to give rise to the unconventional ferroelectricity.

In summary, strong magnetic-lattice-dielectric couplings are found to universally exist in hydroxyl salts $M_2(OH)_3X$, and $M(OH)X$. Further, ferroelectric properties have been found in the deuterated hydroxyl salts $Co_2(OH)_3Cl$ and

$Co_2(OH)_3Br$. Geometrical frustration of the magnetic ions, we think, provides a necessary condition for the unconventional ferroelectricity in that the Co^{2+} ions are geometrically frustrated, therefore, a subtle change in the lattice/bonding breaks the balance and causes dramatic change in their physical properties. Deuteration produces a significant isotope effect on the hydrogen bonds. This work shows the first link between geometrically frustrated magnets and hydrogen-bonded soft-mode ferroelectric materials. Aside from the scientific interest in the mechanism, the present finding is of special interest given that these hydroxyl salts are biomaterials. Therefore, by employing these multiferroic materials, no-hazard grown-in bio-electro-magnetic devices would become possible.

ACKNOWLEDGMENTS

We thank the Japan Society for the Promotion of Science (JSPS) for a Grant-in-Aid for challenging Exploratory Research (Grant No. 22651044), the Ministry of Education, Culture, Sports, Science and Technology (MEXT) for a Grant-in-Aid for Scientific Research on Priority Areas (grant Nos. 20046012 and 22014008). The synchrotron radiation experiments were performed at BL44B2 in SPring-8 with the approval of RIKEN (Proposal No. 20100059, 20110068, and 20120007). We thank Michitaka Takemoto, Seigo Yamamoto for technical support during the synchrotron x-ray diffraction experiment. We are also grateful to Y. Noda and M. Fukunaga at Tohoku University for effort to characterize possible ferroelectrics in $Cu_2(OH)_3Cl$.

---

[*] zheng@cc.saga-u.ac.jp

[1] H. R. von Oswald and W. Feitknecht, Helv. Chim. Acta **47**, 272 (1964).

[2] H. R. von Oswald and W. Feitknecht, Helv. Chim. Acta **44**, 847 (1961).

[3] H. C. Lichtenegger, T. Schöberl, M. H. Bart, H. Waite, and G. D. Stucky, Science **298**, 389 (2002).

[4] L. J. Turbini, Science **298**, 1892 (2002).

[5] X. G. Zheng, T. Mori, K. Nishiyama, W. Higemoto, H. Yamada, K. Nishikubo, and C. N. Xu, Phys. Rev. B **71**, 174404 (2005).

[6] X. G. Zheng, T. Kawae, Y. Kashitani, C. S. Li, N. Tateiwa, K. Takeda, H. Yamada, C. N. Xu, and Y. Ren, Phys. Rev. B **71**, 052409 (2005).

[7] X. G. Zheng, H. Kubozono, K. Nishiyama, W. Higemoto, T. Kawae, A. Koda, and C. N. Xu, Phys. Rev. Lett. **95**, 057201 (2005).

[8] X. G. Zheng, T. Kawae, H. Yamada, K. Nishiyama, and C. N. Xu, Phys. Rev. Lett. **97**, 247204 (2006).

[9] M. Hagihala, X. G. Zheng, T. Toriyi, and T. Kawae, J. Phys.: Condens. Matter **19**, 145281 (2007).

[10] X. G. Zheng, T. Yamashita, M. Hagihala, M. Fujihala, and T. Kawae, Physica B **404**, 680 (2009).

[11] X. G. Zheng, M. Hagihala, K. Nishiyama, and T. Kawae, Physica B **404**, 677 (2009).

[12] M. Fujihala, M. Hagihala, X. G. Zheng, and T. Kawae, Phys. Rev. B **82**, 024425 (2010)

[13] M. Hagihala, X. G. Zheng, T. Kawae, and T. J. Sato, Phys. Rev. B **82**, 214424 (2010).

[14] P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. Lord, A. Amato, and C. Baines, Phys. Rev. Lett. **98**, 077204 (2007).

[15] S. T. Bramwell and M. J. P. Gingras, Science **294**, 1495 (2001).

[16] L. Balents, Nature (London) **464**, 199 (2010).

[17] C. Castelnovo, R. Moessner, and S. L. Sondhi, Nature (London) **451**, 42 (2008).

[18] P. W. Anderson, Science **235**, 1196 (1987).

[19] J. N. Onuchic, Z. Luthey-Schulten, and P. G. Wolynes, Ann. Rev. Phys. Chem. **48**, 545 (1997).

[20] J. J. Hopfield, Proc. Natl. Acad. Sci. USA **81**, 3088 (1984).

[21] K. Kato, R. Hirose, M. Takemoto, S. Ha, J. Kim, M. Higuchi, R. Matsuda, S. Kitagawa, and M. Takata, AIP Conf. Proc. **1234**, 875 (2010).

[22] F. Izumi and K. Momma, Solid State Phenom. **130**, 15 (2007).

[23] X. G. Zheng, C. N. Xu, E. Tanaka, Y. Tomokiyo, H. Yamada, Y. Soejima, Y. Yamamura, and T. Tsuji, J. Phys. Soc. Jpn. **70**, 1054 (2001); X. G. Zheng, Y. Sakurai, Y. Okayama, T. Q. Yang, L. Y. Zhang, X. Yao, K. Nonaka, and C. N. Xu, J. Appl. Phys. **92**, 2703 (2002); H. Yamada, X. G. Zheng, Y. Soejima, and M. Kawaminami, Phys. Rev. B **69**, 104104 (2004).

[24] T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist, and A. P. Ramirez, Nat. Mater. **7**, 291 (2008).

[25] P. M. de Wolff, Acta Crystallogr. **6**, 359 (1953).

[26] J. M. Robertson and A. R. Ubbelohde, Proc. R. Soc. London A **170**, 222 (1939).

[27] X.-Z. Li, B. Walker, and A. Michaelides, Proc. Natl. Acad. Sci. USA **108**, 6369 (2011).

[28] M. I. McMahon, R. J. Nelmes, W. F. Kuhs, R. Dorwarth, R. O. Piltz, and Z. Tun, Nature (London) **348**, 317 (1990).

[29] S. W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13 (2007).

[30] B. B. Van Aken, T. T. M. Palstra, A. Filippetti, and N. A. Spaldin, Nat. Mater. **3**, 164 (2004).

[31] Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T. Arima, and Y. Tokura, Nat. Mater. **8**, 558 (2009).

[32] T. Choi, Y. Horibe, H. T. Yi, Y. J. Choi, Weida Wu, and S.-W. Cheong, Nat. Mater. **9**, 253 (2010).

[33] R. Blinc, B. Zeks, in *Soft Modes in Ferroelectrics and Antiferroelectrics*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1974).

[34] S. Koval, J. Kohanoff, R. L. Migoni, and E. Tosatti, Phys. Rev. Lett. **89**, 187602 (2002); S. Koval, J. Kohanoff, J. Lasave, G. Colizzi, and R. L. Migoni, Phys. Rev. B **71**, 184102 (2005).