Deuterium ordering found in new ferroelectric compound \( \text{Co}_2(\text{OD})_3\text{Cl} \)

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Keywords: deuterium ordering, ferroelectric, geometric frustration, deuteroxyl salt

Abstract

A detailed temperature-dependent Raman spectroscopic study revealed a new type of deuterium-order ferroelectrics in a geometrically frustrated magnet \( \text{Co}_2(\text{OD})_3\text{Cl} \) at \( T_\varepsilon = 229 \) K. Significant changes in the parameters of the Raman vibration modes were observed near \( T_\varepsilon \), suggesting a strong phonon-charge coupling. Additional asymmetric phonon bands appeared below around \( T_\varepsilon \), which are consistently interpreted by phonon folding processes due to a small local structural change resulting from the ordering of deuterium. The wavenumber and intensity changes of the Raman-active modes, as well as the normalized intensities of the additional bands, all follow a power-law fit \( \Delta \omega, \Delta I, I \propto (1 - T/T_C)^{2\beta} \), wherein \( T_C = 230 \) K \( \sim T_\varepsilon \) and \( \beta = 0.35(2) \), clearly demonstrating an ordering process below \( T_\varepsilon \). The critical exponent is reminiscent of a second order transition. Our study presents a rare and new type of multiferroic material with ferroelectricity arising from the deuterium ordering in geometrically frustrated magnets.

1. Introduction

Hydroxyl salts of the type \( \text{M}_2(\text{OH})_3\text{X} \) have been known for a long time \([1]\). In recent years those with the magnetic ions of \( M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+} \) were shown to be geometrically frustrated magnets \([2–10]\), and the substituted compounds of \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) \([11, 12]\), \( \text{ZnCo}_3(\text{OH})_6\text{Cl}_2 \) \([13]\) and \( \text{MgCo}_3(\text{OH})_6\text{Cl}_2 \) \([14]\) showed complete or partial spin liquid features resulting from the geometric frustration. Furthermore, measurements of the lattice parameters and dielectric constants in \( \text{M}_2(\text{OH})_3\text{X} \) revealed simultaneous changes at their respective magnetic transition temperatures, demonstrating that those hydroxyl salts universally have strong magnetic–dielectric lattice couplings \([15]\). In special, the cobalt hydroxyl salts of \( \text{Co}_2(\text{OH})_3\text{Cl} \) and \( \text{Co}_2(\text{OH})_3\text{Br} \), which possess the highest crystal symmetry of \( R3m \) among the hydroxyl salts, showed anomaly in dielectric constants at high temperatures of 229 and 224 K, respectively, when deuterated. Their crystal structure is similar to the spin-liquid compounds \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \), \( \text{ZnCo}_3(\text{OH})_6\text{Cl}_2 \) and \( \text{MgCo}_3(\text{OH})_6\text{Cl}_2 \) by having strong geometric frustration with alternatively stacked layers of regular kagome and triangle lattice planes. Ferroelectric transition was suspected and it was tentatively attributed to the modified hydrogen bonding due to a giant isotope effect, where geometric frustration provided a necessary condition so that a subtle change in the lattice/bonding produced dramatic change in their physical properties in \( \text{Co}_2(\text{OD})_3\text{Cl} \). However, because single crystals are not available at the present time and the usual sintering process cannot be applied to the hydroxyl salts, this subtle ferroelectricity has not been confirmed and its mechanism is unclear.

Ferroelectricity was first discovered in hydrogen-bonded materials and the ferroelectric transitions are characterized as either displacive (such as \( \text{BaTiO}_3 \)) or order-disorder (such as \( \text{NaN}_2O_2 \) or KDP). In recent years, a different type termed as ‘multiferroic’ receives intense attention for scientific interest in their physical properties and potential for applications. Since \( \text{Co}_2(\text{OH})_3\text{Cl} \) and \( \text{Co}_2(\text{OH})_3\text{Br} \) showed magnetic transitions at low temperatures but with strong magnetic couplings even at 400 K \([6, 8, 16]\), if the ferroelectric transition get
confirmed, they can be grouped into multiferroic materials in the wide meaning of multiferroicity. Therefore, they can be viewed as unique multiferroic compounds linking geometric frustration and hydrogen-related ferroelectricity. However, since neither magnetic order nor obvious structure transition exists in this temperature range (e.g. in Co$_2$(OD)$_3$Cl, the ferroelectric response occurs at 229 K, which is much higher than its magnetic transition at $T_N = 10.5$ K) [15], the origin for the observed ‘ferroelectricity’ in this insulating material remains mysterious and demands clarification. On this background, we carried out a detailed temperature-dependent Raman spectroscopic measurement to study the mechanism for the unusual ferroelectricity.

2. Experiments

Polycrystalline Co$_2$(OD)$_3$Cl synthesized using a hydrothermal reaction from CoCl$_2$ and NaOD at around 200 °C, as previously reported, were pressed into a pellet and adhered to a silver plate with silver paste for Raman spectroscopic measurements. The Raman spectra were obtained with a computer-assisted Raman instrument HR800 HORIBA Jobin-Yvon using a special ×50 Olympus objective with an ultra-long working distance to improve the signal-to-noise ratio in the spectra, and a charge-coupled device (CCD) system to collect and process the scattering light. The scattering spectra were excited by a Spectra-Physics model 127 Ar$^+$-ion laser (488.0 nm) with a resolution of 0.5 cm$^{-1}$ between 4000 and 95 cm$^{-1}$. Low temperature measurements were performed using a liquid nitrogen dewar and a helium flow cryostat (Oxford Instruments) equipped with a temperature controller. The temperatures were maintained within a stability of ±0.2 K and a low laser power (5 mW) was used to minimize possible local heating.

3. Results and discussion

3.1. Mode assignment at room temperature

The measured Raman spectra of Co$_2$(OD)$_3$Cl at typical temperatures are plotted in figure 1. Upon cooling to around 230 K, where the ferroelectric response occurred, significant changes in the Raman parameters as described below, as well as additional bands were observed. It is mentioned earlier that Co$_2$(OD)$_3$Cl has the same crystal structure with hydrogenated compound Co$_2$(OH)$_3$Cl, which is a highly symmetric rhombohedral structure in the space group $R3m$ (No. 166) [1]. The magnetic ions Co$^{2+}$ form a three-dimensional network of linked tetrahedron with alternatively stacked layers of regular kagome and triangle lattice planes in the [001] direction. All Co$^{2+}$ ions are surrounded by six ligand ions, and surrounded by four oxygen ions at equal distances and two chlorine ions on the kagome lattice plane. On the other hand, Co$^{2+}$ ion on the triangular lattice plane is surrounded by six oxygen ions at equal distances. Another prominent structural feature is a notable distortion in the tetrahedron that the Co-Co distance on one side of the tetrahedron that has Cl$^-$ ion nearby is 3.42 Å, whereas those on the other three sides bonded with O$^{2-}$ ions are 3.12 Å, indicating a 10% shorter Co-Co distance on the triangular lattice plane [15, 16]. Thus, the symmetries were determined to be $C_{3v}$ for the O site, $C_{3v}$ for the Cl site, $C_{3h}$ and $D_{3d}$ for the Co$^6$ and Co$^5$ sites, wherein Co$^6$ and Co$^5$ denotes the Co$^{2+}$ ions on the kagome and the triangle lattice planes, respectively. Factor group analysis for this structure suggests 12 Raman active modes ($5A_{1g} + 7E_g$) and 17 infrared active modes ($7A_{2u} + 10E_u$), the Raman active modes of Co$_2$(OD)$_3$Cl are labeled M1 to M12. According to the previously reported assignment results of Co$_2$(OH)$_3$Cl/Br [17, 18], and Cu$_2$(OH)$_3$Cl [19], the Raman spectra could be separated into four regions.

![Figure 1. Raman spectra of Co$_2$(OD)$_3$Cl at typical temperatures.](image-url)
Table 1. Twelve Raman active modes and eight additional bands in Co$_2$(OD)$_3$Cl and their band positions observed at 200 K. The numerals in the parentheses for the new bands are calculated values for the overtone and combined modes at 200 K.

| Raman active bands | Vibration modes |
|--------------------|----------------|
| No. | Band positions (cm$^{-1}$) at 200 K | |
| M1 | 2633 | $A_{1g}$(OD) symmetric stretching |
| M2 | 2625 | $E_g$(OD) antisymmetric stretching |
| M3 | 627 | $A_{1g}$(OD) symmetric bending |
| M4 | 528 | $E_g$(OD) antisymmetric bending |
| M5 | 483 | $E_g$(OD) antisymmetric bending |
| M6 | 452 | $A_{1g}$(Co$_3$O(D)) symmetric stretching |
| M7 | 417 | $A_{1g}$(Co$_3$O(D)) symmetric bending |
| M8 | 393 | $E_g$(Co$_3$O(D)) antisymmetric bending |
| M9 | 330 | $E_g$(Co$_3$O(D)) antisymmetric stretching |
| M10 | 245 | $E_g$(Co$_3$O(D)) antisymmetric bending |
| M11 | 170 | $A_{1g}$(Co$_3$Cl) symmetric stretching |
| M12 | 134 | $E_g$(Co$_3$Cl) symmetric bending |
| N1 | 1356 | 3M$_6$(1356) |
| N2 | 1286 | M$_6$ + 2M$_7$(1286) |
| N3 | 1256 | 2M$_3$(1254) or 3M$_7$(1251) |
| N4 | 1202 | M$_7$ + 2M$_8$(1203) |
| N5 | 1143 | 2M$_6$ + M$_{10}$(1149) |
| N6 | 925 | 3M$_7$-M$_9$(921) |
| N7 | 813 | M$_7$ + M$_8$(810) |
| N8 | 299 | 2M$_9$-M$_6$(208) |

(1) [OD] function group (FG) region: 3000–2000 cm$^{-1}$;

(2) [OD] correlation peak (CP) region: 800–450 cm$^{-1}$;

(3) [Co$_3$O(D)] fingerprint-1 (FP1) region: 450–200 cm$^{-1}$;

(4) [Co$_3$Cl] fingerprint-2 (FP2) region: <200 cm$^{-1}$.

The assignment of various modes of Co$_2$(OD)$_3$Cl could been done as follows.

In the [OD] function group (FG) region, there are M1 (2630 cm$^{-1}$) and M2 (2620 cm$^{-1}$) two Raman bands with peak separations of several cm$^{-1}$. From the fact that all red-shift ratios are close to the theoretical value $[\mu_{\text{OH}}/\mu_{\text{OD}}]^{1/2} = 72.8\%$ (here, $\mu_{\text{OH(D)}}$ is the [OH/D] reduced mass), M1 and M2 can be safely assigned to [OD] stretching modes.

The small band at 3555 cm$^{-1}$ was confirmed to be due to contamination of a small amount of hydroxyl (strength ratio $I_{\text{OH}}/I_{\text{OD}} \sim 3\%$). The bands at 1600 and 1475 cm$^{-1}$ (as denoted by asterisks) also exist in Co$_2$(OH)$_3$Cl, we could assign them to the combinations of multi-phonon modes, which are correlated with the residual H nuclei.

In the [OD] correlation peak (CP) region, there are M3–5 (620, 520, 480 cm$^{-1}$) three Raman bands. According to the fact that all redshift ratios are close to the theoretical value 72.8%, M3–5 are reasonably assigned to the [OD] bending modes. The band at 690 cm$^{-1}$ can be assigned to the [OH] bending vibration that originating from the residual H.

For the fact that O ions are moving along with D ions as a whole group [OD] in the [Co$_3$O(D)] fingerprint-1 (FP1) region, and the redshift ratios are also close to the theoretical value $[17/18]^{1/2} = 97.2\%$, so M6-10 (445, 413, 386, 323, 243 cm$^{-1}$) can be assigned to [Co$_3$O(D)] vibrations.

The remaining two band M11 (165 cm$^{-1}$) and M12 (130 cm$^{-1}$) can be determinately assigned to [Co$_3$Cl] vibrations, compared with the bands (148/123 cm$^{-1}$) assignments in Herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$ [20]. The assignment of the main modes has been summarized in table 1, and the mode displacements are illustrated in figure 2.

3.2. Evolution of Raman modes with temperature

The Raman scattering profile has been fitted using a Lorentz function to compute the exact wavenumber (Raman shift), line-width (full width at half maximum, FWHM) and intensity of each peak. In figures 3–5, we showed the temperature dependence of the wavenumbers, line-widths and integrated intensities for the selected M3, M8 and M11 Raman-active modes, which are correlated with the [OD], [Co$_3$O(D)] and [Co$_3$Cl] units’ vibration, respectively. In general, as the temperature decreases, the lattice modes tend to harden and their line-
Figure 2. Illustration of the directions (denoted by the arrows) of the Raman mode displacements in Co$_2$(OD)$_3$Cl. The D, Co, O and Cl ions are presented by purple, black, blue and green balls (in the sequence from small to large radius).

Figure 3. Temperature dependence of the wavenumber (cm$^{-1}$) and wavenumber difference (cm$^{-1}$) for the Raman-active modes M3, M8 and M11.

Figure 4. Temperature dependence of the FWHM (cm$^{-1}$) for modes M3, M8 and M11.
widths decrease as a result of anharmonic effects and thermal changes. Here, we tried to fit the wavenumber and line-width variations using conventional formulae with lattice and phonon-phonon anharmonic interaction processes up to three phonons [21]:

\[
\omega(T) = \omega_0 + A \left[ 1 + \frac{2}{e^x - 1} \right] + B \left[ 1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right]
\]

\[
\Gamma(T) = \Gamma_0 + C \left[ 1 + \frac{2}{e^x - 1} \right] + D \left[ 1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right]
\]

Here, \(x = \frac{hc \omega_0}{2k_B T}\) and \(y = \frac{hc \omega_0}{3k_B T}\). As shown in figure 3, the wavenumber at high temperatures could be well fitted by the anharmonic equation. However, the selected modes showed clear deviation from the fitted curves below \(T_c\), suggesting that there are additional interactions besides the expected lattice and phonon-phonon interaction. In order to explore the correlation between the vibrational and structural changes, we also considered the temperature dependence of the wavenumber differences for these modes. The temperature dependence of the wavenumber difference \(\Delta \omega_3, \Delta \omega_8\) and \(\Delta \omega_{11}\) for mode M3, M8 and M11 between the observed and extrapolated wavenumbers below \(T_c\) could be well expressed in a power-law equation like that in the displacive-type ferroelectric \(\text{Sn}_2\text{P}_2\text{Se}_6\) [22]. As exemplified in figure 3, the difference \(\Delta \omega_3, \Delta \omega_8\) and \(\Delta \omega_{11}\) increased abruptly from \(T_c\), following the equation \(\Delta \omega \propto (1 - T/T_c)^\beta\) with \(T_c = 230\,\text{K} \sim T_c\), \(\beta = 0.35(2)\) (\(\beta\) is the critical exponent for the order parameter, the error of the critical exponent is from the upper and lower limits in the fitting process). This suggests a subtle local structural change below \(T_c\). Since the present material is geometrically frustrated, the variation in local [OD] unit vibration (M3) will induce subtle changes in the integral structure. Thus, [Co3O(D)] unit (M8) and [Co3Cl] unit (M11) exhibited nearly the same variation with that in the [OD] unit. The line-widths for these modes especially M8 involving the magnetic Co2+ ions, showed obvious anomalies near \(T_c\) deviating from the expected behavior, as illustrated in figure 4. In general, the change in Raman parameters with temperature can be caused by several factors, such as phonon-phonon anharmonic interaction, spin-phonon coupling, or phonon renormalization resulting from electron-phonon coupling [23, 24]. The latter one can be neglected when the carrier concentration is low. Since the line-widths are not susceptible to the subtle lattice volume changes due to magnetostriction, the variation in the line-width of M8 should be induced by the spin-phonon coupling. This result is needed to be confirmed by further studies.

Since the Raman scattering intensity is susceptible to the change of ferroelectricity, we also considered the integrated intensities and intensity differences below \(T_c\) for the selected modes. As shown in figure 5, the intensities below \(T_c\) deviated from the straight lines extrapolated from the data above \(T_c\) and saturated toward 150 K. The intensity difference (absolute value) \(\Delta I_3, \Delta I_8\) and \(\Delta I_{11}\) between the observed and extrapolated intensities can be well fitted in the same way as that in the well-known proton-ordering ferroelectric PbHPO4 [25] and order-disorder ferroelectric NaNO3 [26, 27], similarly following the power-law expression \(\Delta I \propto (1 - T/230)^{2\alpha}\). The results suggest an ordering process below \(T_c\) accompanying the appearance of ferroelectricity. This ordering is strongly coupled with the Co tetrahedron, and gives rise to the structural change.
Direct evidence for the transition near 230 K appeared as the additional spectral bands labeled N1 to N7, as shown in figure 1, which are highly asymmetric in their line shapes. The Raman spectra of Co2(OH)3Cl (not shown here), measured at the same conditions as that on the deuterated compound, showed no additional spectral bands as on the deuterated one in the same frequency and temperature ranges. Thus, considering the fact that their lattice structures are quite the same, it is apparent that these additional bands below 230 K on Co2(OD)3Cl have close relation with the deuterium motion. Asymmetric Raman line shapes have once been attributed to a Fano effect, which are often found in charge-ordered ferroelectric semiconductors [29]. The temperature-dependent normalized intensities for the additional bands in the present material, as illustrated in figure 6, can also be well fitted by the above ordering expression $I \propto (1 - T/T_C)^{2\beta}$. Apparently, the intensities of the additional bands could be used conveniently to describe the ordering process for the ferroelectric transition below $T_C = 230$ K, as in other materials [22, 25–27]. The additional bands arising below 230 K might be infrared active modes, which become Raman active due to the symmetry breaking at the phase transition. Inspection of their frequencies suggests that the additional bands can be assigned to the combination or overtone of anharmonic vibrations of the [Co3O(D)] units, as shown in table 1. This kind of anharmonic overtone and combination were rare, however, they have been observed in a proton-ordering ferroelectric material NaNH4SO4·2H2O [28]. The fact of the occurrence of ferroelectricity with deuteration in Co2(OD)3Cl and the overtone and combination of the [Co3O(D)] unit modes strongly suggest a kind of deuterium ordering near the $T_C$. Thus, the additional asymmetric bands, as well as the prominent changes of the selected modes can be consistently explained by changes in lattice and anharmonicities arising from the deuterium ordering in the insulating Co2(OD)3Cl. Several additional modes are still recognizable in the paraelectric phase at 240 K, showing remaining phonon–charge couplings as observed in proton-ordering ferroelectric compounds [25].

Through the analyses in the present work, we obtained the critical exponent $\beta = 0.35(2)$. As is well known, second order phase transitions follow a power-law expression with universal critical exponents, wherein the $\beta$ values are calculated to be around 0.31 $\sim$ 0.35 for different models [30]. The present $\beta$ value is consistent with the value predicted for intrinsic second-order transitions. This interpretation is consistent with the experimental facts that no obvious structural phase transition was observed in the present material. On the other hand, rearrangement of all [OD], [Co3O(D)] and [Co3Cl] units occurred accompanying the D sub-lattice ordering. This kind of rearrangement, we suspect, gave rise to the ferroelectricity. The nature of the ferroelectric phase transition in the present material is nearly the same as that showed in KDP, wherein both displacive and order-disorder type transitions were involved.

Another relevant feature is the temperature dependence of a band at $\sim 210$ cm$^{-1}$ (marked by the vertical arrows in figure 1) in the vicinity of the mode M10. This band decreased upon heating and completely disappeared at about 150 K. This change, together with the tendencies of saturated wavenumbers and intensities of the phonon modes at lower temperatures (see figures 3 and 5), may suggest that the system reached a new equivalent state for the deuterium ordering below 150 K. This feature deserves further investigation.
4. Conclusion

In summary, strong evidences of deuterium-order ferroelectricity in compound $\text{Co}_2(\text{OD})_3\text{Cl}$ are obtained from a Raman spectroscopic study. A critical scaling is found near the $T_c \sim 230$ K with a critical exponent $\beta = 0.35(2)$, suggesting a second order transition. Since prominent changes occurred in the $A_{1g}$ and $E_g$ modes associated with $D$ and $O$, the deuterium ordering should occur near the three side planes of the Co tetrahedron in the structure. This ordering is strongly coupled with the lattice vibration modes involving the $[\text{Co}_3\text{O(D)}]$ units, and would bring out a structural transition, as is exemplified in the well-known ferroelectric KDP. However, the structural change in $\text{Co}_2(\text{OD})_3\text{Cl}$ should be exceptionally small or unusual, thus it was overlooked in previous structural studies. The present work shows that $\text{Co}_2(\text{OD})_3\text{Cl}$ can be viewed as a unique prototypical multiferroic compound combining the geometric frustration and deuterium ordering ferroelectricity. The present material should belong to the mixed-type ferroelectrics that an ordering arrangement of deuterium and an instability of the lattice vibration occur simultaneously, thus manifesting both the displacive-type and order-disorder type ferroelectric features.

Acknowledgments

This work is supported by the Grant-in-Aid for challenging Exploratory Research (grant No. 25630128), Grant-in-Aid for Scientific Research (B) (grant No. 26289092) to X.G.Z. from the Japan Society for the Promotion of Science (JSPS) and partly supported by competing research grant from the Dean of the Graduate School of Science and Engineering, Saga University.

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