Raman Spectroscopic Study on the Ferroelectricity in Multiferroic Materials CuO and Co$_2$(OH/D)$_3X$

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Chapter 1. Introduction

Abstract. Some elementary physical theories, as well as the structural and magnetic properties of the materials related to this dissertation were introduced.

Contents. Solid state physics mainly studies the properties of structure, mechanics, thermos, electric, magnetism, and optics of the crystalline and non-crystalline solids. It is the largest branch of condensed matter physics.

Ferroelectricity is a property of certain materials with a spontaneous electric polarization. According to the different induced mechanisms, the ferroelectrics can be classified into many different types, such as displacive-type, order-disorder-type, hydrogen-bonded KDP-type ferroelectric, as well as magnetically driven and charge ordering induced ferroelectrics. Ferroelectricity is an important property in multiferroics, this dissertation mainly focuses on the mechanisms of the ferroelectricity in multiferroic materials CuO and Co$_2$(OH/D)$_3$X ($X = \text{Cl, Br}$).

The growth of single crystal CuO is using the chemical vapor transport method \[1\]. It crystallizing in a monoclinic structure is described by the space group $C_{2h}^6$ ($C2/c$ no.15) and featured by distorted octahedrons with Cu atoms at the center, as shown in Fig. 1-1.

![Fig. 1-1. Crystal structure of CuO. Here, small blue balls: Cu$^{2+}$ ions; large red balls: O$^{2-}$ ions.](image)

Previous research on CuO has clarified two successive magnetic transitions in CuO: antiferromagnetic ordering at $T_{N1} = 230$ K followed by helical to commensurate ordering with spin reorientation at $T_{N2} = 213$ K \[2\], and the ferroelectricity exists in the intermediate phase between $T_{N1}$ and $T_{N2}$ \[3\].

The synthesis of polycrystalline Co$_2$(OH/D)$_3$X is using the hydrothermal solution reaction method \[4\]. They have the same crystal structure with rhombohedral structure.
in the space group $\overline{Rm}$ (no. 166) at room temperature, the magnetic ions Co$^{2+}$ in Co$_2$(OH)$_3$X form a three-dimensional network of linked tetrahedron with alternatively stacked layers of regular kagome and triangle lattice planes along the [001] direction \cite{4}, as shown in Fig. 1-2.

![Fig. 1-2. The crystal structure of Co$_2$(OH/D)$_3$X at room temperature. The H/D, Co, O and X (X = Cl, Br) ions are presented by purple, black, blue and green balls (in the sequence from small to large radius) (Image)](image)

It has been reported for Co$_2$(OH)$_3$Cl that below $T_N = 10.5$ K, only the Co$^{2+}$ spins on the triangular-lattice plane order ferromagnetically and the Co$^{2+}$ spins on the kagome-lattice plane remain to be disordered, showing partial ferromagnetic order together with slow spin dynamics \cite{5}. The recent measurements on the cobalt hydroxyl salts of Co$_2$(OH)$_3$Cl and Co$_2$(OH)$_3$Br showed prominent ferroelectric-like responses at high temperatures $T_e = 229$ K and 224 K, when deuterated, respectively \cite{6}.

**Motivation.** 1. Magnetism-induced ferroelectricity is one important feature of the magnetoelectric multiferroic materials. The strongly coupled ferroelectric and ferromagnetic (antiferromagnetic) order parameters are promising for developing new devices with both electrical and magnetic controllability. On the basis of the dielectric and magnetic measurements, the author mainly performed Raman spectroscopic measurement on high-quality single crystal CuO, to make a grasp of the multiferroicity of CuO and the mechanism of magnetism-induced ferroelectricity.

2. The ferroelectric responses of Co$_2$(OD)$_3$X were tentatively attributed to the modified hydrogen bonding due to a drastic isotope effect. However, because the single crystals are not available for measurements at the present time and the usual sintering process cannot be applied to the present hydroxyl salts, this subtle
ferroelectricity has not been confirmed and its mechanism is unclear. The author mainly carried out the detailed temperature-dependent Raman spectroscopic measurements on Co₂(OH/D)_3X to explore the occurrence of ferroelectricity, as well as its induced mechanism.

Reference.

Chapter 2. Experimental Methods

Abstract. In this chapter, the principle of Raman effect, the descriptions and applications of Raman spectroscopy were introduced in detail, as well as the low-temperature measurement processes on single crystal CuO and polycrystalline Co$_2$(OH/D)$_3$X.

Contents. Raman effect was first discovered by Indian scientist C. V. Raman in 1928. Raman spectroscopy is one of the spectroscopic techniques, which is complementary with infrared absorption and can be used to detect vibrational and rotational modes related with the component atoms, as well as low-frequency transitions in a system [1]. It relies on inelastic scattering feature (or say, Raman scattering) of monochromatic light, the incident laser light interacts with molecular vibrations, phonons or other excitations (for example, electronic or magnetic excitation) in the system, resulting in the energy of the incident laser photons being changed. The energy change will give information about the vibrational modes (molecular bonds) of the system.

Raman signal is normally quite weak. Until to now, many efforts have been done to enhance the intensity of Raman signals. There are a number of advanced types of Raman spectroscopy have been developed to enhance the sensitivity (e.g., surface-enhanced Raman), to acquire specific information (e.g., resonance Raman), or to improve the spatial resolution (e.g., Raman microscopy), and so on [2].

The works related to this dissertation were carried on using the confocal microscopic Raman spectroscopic instrument. 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. The scattering spectra were excited by a Spectra-Physics model 127 Ar$^+$-ion laser (488.0 nm (20492 cm$^{-1}$)) with a resolution of 0.5 cm$^{-1}$ between 4000 and 95 cm$^{-1}$.

For the Raman spectroscopic measurement on single crystal CuO, since the incident light is unpolarized, the CuO crystal with large (001) plane was used for measurement. The sample was pasted into the susceptor using conductive adhesive (APIEZON for low temperature) or silver paste. Meanwhile, for the polycrystalline Co$_2$(OH/D)$_3$X, the powder samples need to be pressed into pellets beforehand, and the pellet is adhered to a silver or copper plate with silver paste for measurements.

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 (10 mW for CuO, 5 mW for Co₂(OH/D)₃) was used to minimize possible local heating.

Reference.

Chapter 3. Multiferroicity in single crystal CuO

Abstract. Dielectric constant and Raman spectroscopic measurements on single crystal CuO were performed at temperatures between 77 and 290 K. Through dielectric measurements, dielectric anomalies at two successive magnetic transition temperatures 230 K and 213 K were observed along the three crystal axes. Beside of the appearance of the additional band at low temperatures, which is consistent with the previously reported lattice stiffen near 170 K, the temperature dependence of the Raman parameters of the Raman-active modes revealed anomalous behaviors near the magnetic transition temperatures which are considered to be correlated with the multiferroic transition.

Results and discussion.

Fig. 3-1. Temperature dependences of the real part ($\varepsilon'$) of the dielectric constants along the a, b, c-axis directions ($f = 100$ KHz), respectively.

Fig. 3-1 shows the anisotropic dielectric variations along the three crystal axes. One can observe the dielectric anomalies at the two successive magnetic transitions $T_{N1}$ and $T_{N2}$ along three different crystal axes. In special, a steep step-like drop at $T_{N2}$ along the c-axis direction were also observed. It has been known that the multiferroicity occurs in the temperature range $T_{N1} < T < T_{N2}$. The most obvious dielectric anomaly occurred along the b-axis at $T_{N1}$. Combining with the previous susceptibility measurements, the
anomalies at $T_{N1}$ and $T_{N2}$ in the dielectric constants are identified to directly reflect the occurrence of multiferroicity resulting from the helical spin ordering between $T_{N1}$ and $T_{N2}$ [1].

Anomalies in lattice vibrations were also investigated using Raman scattering as a function of temperature to understand the high-$T_C$ multiferroic properties of CuO. An additional phonon mode below $T_{N2}$ was observed, its frequency change and normalized intensity all follow a power-law fit $\Delta \omega, I \propto (1 - T / T_C)^{2\beta}$ [2, 3], wherein $T_C = 170 \text{ K} < T_{N2}$ and $\beta = 0.35(2)$, as shown in Fig. 3-2. This result is consistent with the previous suggestion that lattice stiffens below 170 K, and can be interpreted as a second-order transition below $T_{N2}$, which may be attributed to the structure distortion accompanying magnetic ordering.

![Fig. 3-2. Temperature dependence of (a) the frequency change, and (b) the intensity (normalized by the respective intensities at 77 K) for the additional Raman band.](image)

Variations in the temperature-dependent frequency changes of the three Raman-active phonon modes exhibited obvious structural change around 235 and 215 K, as shown in Fig. 3-3, which are in rough agreement with the magnetic phase transition temperatures. Simultaneously, anomalies in the line-widths of the $B_{g1}$ and $B_{g2}$ modes were also observed, suggesting a strong spin-phonon coupling arising from the magnetic ordering. The intensity variations in the $B_{g1}$ and $B_{g2}$ modes were confirmed to have homologous relation with the ferroelectricity. The author concluded that the magnetic order in the intermediate phase brought out the distortion of CuO$_6$ octahedron without centro-symmetry as that in the multiferroic materials $R$CrO$_3$ [4] and $R$MnO$_3$ [5], then giving rise to the ferroelectricity.
**Conclusion.** The present Raman measurement shows an additional band at low temperatures, which is consistent with the previous suggestion that the lattice tend to stiffen below 170 K. Obvious variations were observed in the evolution of the Raman parameters of the $B_{g1}$ and $B_{g2}$ modes near the magnetic transition temperatures, which were mainly caused by the spin-phonon coupling and magnetic-induced lattice distortion. Because of the antiferromagnetic ordering accompanying with the incommensurate helical magnetic ordering in the intermediate phase, the spin-phonon coupling effect displaced the magnetic Cu$^{2+}$ ions, the Cu-O bond length and bond angle exhibited subtle changes giving rise to the distortion of CuO$_6$ octahedron, then inducing the coexistence of antiferromagnetism and ferroelectricity.

**Reference.**


Chapter 4. Ferroelectricity verified in new compounds Co$_2$(OH/D)$_3$X

Abstract. Detailed measurements were performed on the geometrically frustrated magnets Co$_2$(OH/D)$_3$X to reveal the mysterious origin of their ferroelectric responses. For the deuterated salt Co$_2$(OD)$_3$Cl, significant changes in the parameters of the Raman-active modes were observed near $T_c$, suggesting a strong phonon-charge coupling. Additional asymmetric phonon bands appeared below around $T_c$, which are consistently interpreted by phonon folding processes due to a small local structural change resulting from the ordering of deuterium. The frequency 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 $\sim T_c$ and $\beta = 0.35(2)$, clearly demonstrating an ordering process below $T_c$. The critical exponent is reminiscent of a second order transition. At the same time, the same analysis methods were used on the other of this series of materials, and suggested that the hydrogen (proton/deuterium) order-induced frustrated ferroelectric transition in different way and at different temperature, due to the drastic isotopic effect and bond length difference.

Results and discussion. For the deuterated salt Co$_2$(OD)$_3$Cl, the Raman frequency changes of the selected Raman-active modes between the observed and extrapolated values below $T_c$ all follow a power-law fit $(1 - T / T_C)^{2\beta}$ like that in the displacive-type ferroelectric Sn$_2$P$_2$Se$_6$ [1] with $T_C = 230$ K $\sim T_c$, $\beta = 0.35(2)$, as shown in Fig 4-1, suggesting a subtle local structural change below 230 K. The Raman scattering intensity differences between the observed and extrapolated values can be well fitted in the same way as that in the well-known proton-ordering ferroelectric PbHPO$_4$ [2] and order-disorder ferroelectric NaNO$_3$ [3], similarly following the power-law expression $(1 - T / T_C)^{2*0.35}$, as shown in Fig 4-2, suggesting an ordering process accompanying the appearance of ferroelectricity below 230 K. This ordering is strongly coupled with the Co tetrahedron giving rise to the structural change.

The temperature-dependent normalized intensities for the additional bands can also be fitted by the above ordering expression $(1 - T / T_C)^{2*0.35}$, as shown in Fig. 4-3. Apparently, the intensities of the additional bands could be used conveniently to describe the ordering process for the ferroelectric transition below $T_C$. 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. Another relevant feature is the temperature dependence of the band DN8, which is a shoulder band of D10 at high temperatures, and becomes visible below about 150 K. This change, together with the tendencies of the saturated frequencies and intensities of the Raman-active modes at lower temperatures, may suggest that the system changed to a new equivalent state for the deuterium ordering below 150 K.

![Temperature dependence of the frequencies and frequency differences](image)

**Fig. 4-1.** Temperature dependence of the frequencies and frequency differences for the selected Raman-active modes D3, D10 and D11 in Co₂(OD)₃Cl, respectively.

![Temperature dependence of the intensities and intensity differences](image)

**Fig. 4-2.** Temperature dependence of the intensities and intensity differences for the selected Raman-active modes D3, D10 and D11 in Co₂(OD)₃Cl, respectively.
Fig.4-3. Temperature dependence of the intensities for the additional bands DN1-DN8 in Co$_2$(OD)$_3$Cl. DN1-DN7 in Co$_2$(OD)$_3$Cl follow the power-law expression $I \propto (1–T/230)^2*0.35(2)$, while DN8 shows variations near 230 K and 150 K.

At the same time, the same analysis methods were used on the hydrogenated salt Co$_2$(OH)$_3$Cl, and suggested that the hydrogen (proton) order-induced ferroelectric transition in different way and at different temperature, due to the drastic isotopic effect. The same analysis methods were also used to explore the ferroelectric anomalies in Co$_2$(OH/D)$_3$Br. The author obtained preliminary results about the hydrogen (proton/deuterium, H/D) ordering inducing the ferroelectric transition. Because the Co-Co bonding length on the kagome lattice plane is much longer in the bromated salts, the hydrogen (H/D) order-induced ferroelectric transitions at different temperatures comparing with that in the chlorinated salts Co$_2$(OH/D)$_3$Cl.

The ferroelectric phase transitions could be considered to be second-order, and the spatial group of the crystal should change slightly from $R\overline{3}m$ to $R3m$ below $T_C$.

**Conclusion.** Strong evidences of deuterium-order-induced ferroelectricity in compound Co$_2$(OD)$_3$Cl were 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 Raman-active 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 [Co$_3$O(D)] units, and would bring out a structural transition, as is exemplified in the well-known ferroelectric KDP. However, the structural change in Co$_2$(OD)$_3$Cl should be exceptionally small or unusual, thus it
was overlooked in previous structural studies. The present work shows that Co$_2$(OD)$_3$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.$^{[4]}$

In summary, the studied salts Co$_2$(OH/D)$_3$X are isostructural, exhibit very similar physical properties that hydrogen (H/D) ordering inducing the ferroelectricity with a second-order phase transition at different temperatures due to the drastic isotopic effect and bond length difference. The present ferroelectric transitions could be considered to be frustrated. The detailed conclusions about the other materials of the series of Co$_2$(OH/D)$_3$X will be described later.

Reference.

Chapter 5. Conclusions

Conclusions. According to the series of experimental results about the single crystal CuO and polycrystalline Co$_2$(OH/D)$_3$X, the conclusions can be summarized into two parts, mainly based on the Raman spectroscopic measurements:

Part 1: A Raman scattering study of single crystal CuO in the temperature range of 290 – 77 K was presented in the first part. The present Raman results exhibited an additional band at low temperatures, which may be induced by the structural change accompanying magnetic ordering below $T_{N2}$. The critical constant $\beta$ exhibits that this change is small and can be considered to be second order.

Obvious anomalies were also observed in the evolution of the Raman parameters of the $B_{g1}$ and $B_{g2}$ modes near the magnetic transition temperatures, which were mainly caused by the spin-phonon coupling and magnetic-induced lattice distortion. Because of the antiferromagnetic ordering accompanying the incommensurate helical magnetic ordering in the intermediate phase, the spin-phonon coupling effect displaced the magnetic Cu$^{2+}$ ions, the Cu-O bond length and bond angle exhibited subtle changes giving rise to the distortion of CuO$_6$ octahedron, then inducing the multiferroic feature, i.e., the coexistence of antiferromagnetism and ferroelectricity.

Part 2: The studied polycrystalline salts Co$_2$(OH/D)$_3$X are isostructural, exhibit very similar physical properties that hydrogen (H/D) ordering inducing the ferroelectricity, and undergo analogous phase transition at different $T_C$, but the ferroelectricity arise in different ways. The present results suggested that the deuterium ordering subsequently affected the lattice vibration modes at 230 K in Co$_2$(OD)$_3$Cl, involving the [Co$_3$O(D)] and [Co$_3$Cl] units and brought out the structural transition, then inducing the ferroelectricity. And a more stable equivalent state established below about 150 K in Co$_2$(OD)$_3$Cl.

A critical scaling is found near the $T_e \sim 230$ K with a critical exponent $\beta = 0.35(2)$, suggesting a second order transition. Since the emergence or disappearance of ferroelectricity is always accompanied by the change of lattice structure, Zheng’s group has carried out neutron diffraction studies and found that the present spatial group symmetry should change slightly from $R\overline{3}m$ to $R3m$ with polarity below $T_C$, which is consistent with the symmetry relations between space groups. However, the structural changes are exceptionally small or unusual, thus they have been overlooked in previous structural studies.
The present works verified the concept proposed by Zheng that the Co$_2$(OH/D)$_3$Y compound can be viewed as unique prototypical multiferroic compounds combining the geometric frustrated (anti)ferromagnetism and hydrogen (H/D) isotopic ordering ferroelectricity. Due to the drastic isotope effect, the proton- and deuterium-order-induced ferroelectric phase transition at different temperatures, as that in the hydrogen-bonded KDP-type ferroelectrics, wherein both the displacive and order-disorder transitional natures were all involved.