

## 別紙 1 (博士論文の審査結果の要旨)

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In recent years, geometrically frustrated magnets receive intense attention because they are playgrounds for unconventional quantum states such as spin liquid and other novel properties. Many exotic quantum magnetic phenomena related to the magnetic geometrical frustration (MGF) have been found and studied in several kinds of uniformly crystallized materials, including the hydroxyl chlorides  $M_2(\text{OH})_3X$  series. Because there is the existing spin-lattice coupling effect in the MGF system, it should be possible to probe the magnetic properties through measuring the lattice vibration (phonon) features accompanied with dynamic coupling to spin interactions by using infrared (IR) and Raman spectroscopic technologies. Till now, although there have been a lot of research on the relationship of crystal lattice and magnetism, few have been conducted on their dynamic coupling. In this work, evaluation of the dynamic coupling, as is exemplified in the  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ , is the final research aim.

To reach this aim, the author of this dissertation has performed a standard factor group analysis on all four kinds of space groups to which the all geometrically frustrated transition-metal hydroxyl halides  $M_2(\text{OH})_3X$  ( $M=\text{Co, Ni, Cu}$ ;  $X=\text{Cl, Br}$ ) belong, measured the IR and Raman spectra at room temperature (RT) and assigned almost all the normal modes as complete as possible, and conducted the low-temperature Raman scattering experiments on several samples to investigate their Raman

spectroscopic response to the MGF properties. The structure of this dissertation is as the following:

In Chapter 1, some elementary physical topics related to the dissertation and research situation of spectral studies on hydroxyl halides are introduced, and then research aims and methods of the doctoral dissertation are given in detail.

In Chapter 2, the author has performed, for the first time to the best of our knowledge, a standard factor group analysis on the space groups of No. 166, No. 62, No. 14 and No. 11, through working out corresponding point group character and correlation tables by considering carefully all cite symmetric species. These have built up the foundation to the complete normal mode assignment.

In Chapter 3, the author has performed spectral analysis of IR and Raman spectra of most of hydroxyl halides  $M_2(\text{OH})_3X$  at RT. The following results have been obtained:

(1) Using five spectral analyzing methods, it is found that the whole IR or Raman spectrum of each sample can be divided into four well-separated regions: [OH/D] function group, [OH/D] correlation peak,  $M\text{-O}$  and  $M\text{-X}$  fingerprint regions, respectively. In addition, wrong assignments of some bands in previous publications are pointed out.

(2) In each spectral region, most experimental spectral bands have been assigned definitely and are considered to correspond well to their normal modes predicted by the standard FGA method. From those sharp band profiles in each spectrum, it is concluded that each sample is well crystallized and suitable for the further spectral

study.

(3) After checking the [OH] stretching frequency of each sample and its crystal structure, three kinds of  $(\text{OH})_3 \cdots X$  hydrogen bond (H-bond) are found to exist in these materials according to the structural symmetry, and they have been nominated trimeric H-bond by our research team. The trimeric H-bonds in this series are found to have four subtypes and two more subtypes are predicted to exist in nature.

(4) Furthermore it is found that the trimeric H-bond concept and the approximate linearity between the [OH] stretching frequency and [OH] distance can be applied to estimate and evaluate the rightness of the OH distances given by other authors, and determine the difference between different OH groups, *etc.*

In Chapter 4, through the temperature-dependent Raman spectroscopic investigation on the clinoatacamite  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ , the following results are obtained and given:

(1) Among eight representative normal modes, the trend as a whole of five frequency variations and all eight width variations in the wide-temperature range presents a normal thermal expansion behavior of a normal non-magnetic and isolating material. Yet each of the other three frequency variations shows an abnormal behavior, and it has been elucidated by the dominating effect of the trimeric H-bond.

(2) It is found that the commonly used fitting formula of both frequency and width variations resulting from the sum of lattice and phonon-phonon anharmonic terms at the high-temperature are not suitable for fitting the high frequency modes.

(3) Obvious Raman spectroscopic evidences of

successive magnetic transition are found at the Curie temperatures  $T_{c1}=18$  K and  $T_{c2}=6$  K: it comes from the apparently anomalous temperature-dependent Raman band frequencies and linewidths of 8 modes below about 18 K because of spin-phonon coupling effect.

(4) Based on the quantitative analysis on the pronounced background at high-temperature and the broad continuum at the intermediate and low-temperatures, it is verified that the coexistence of partial magnetic order and spin fluctuations of a picosecond time scale at the intermediate phase in the temperature range of  $T_{c1}=18$  K and  $T_{c2}=6$  K comes from quasi-two-dimensional antiferromagnet lattice structure.

In Chapter 5, the above-mentioned works are concluded, and an outlook is given.

In summary, the author has obtained several achievements in respect of the dynamic coupling of lattice vibration and the magnetism in the geometrically frustrated  $M_2(\text{OH})_3X$  series. In particular, the low-temperature investigation of  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  of Raman spectra has given the spectral evidence of the successive magnetic transitions and revealed the nature of coexistence of magnetic order and spin fluctuations in the intermediate phase between  $T_{c1}$  and  $T_{c2}$ . Unpolarized Raman scattering can only provide limited information about the dynamic coupling, therefore, it is hoped that further experiments of polarized Raman scattering experiments on single crystals be performed to completely uncover the exotic nature of the frustrated magnetism in the hydroxyl chlorides  $M_2(\text{OH})_3X$  series.