論 文 内 容 要 旨

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学位論文の題　　目	Magnetoelectric response in honeycomb antiferromagnets （ハニカム反強磁性体における磁気電気応答）		

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Abstract

In strongly correlated materials, the competition and cooperation between different degrees of freedom, such as charge, spin and lattice, lead to several interesting and complicated phenomena. Among them, the coupling between different ferroic orders, which is known in term multiferroic, has archived huge attention due to their intriguing in fundamental physics as well as possibility for application in multi-functional electronic devices. Magneto-electric (ME) effect occurs in the system where time reversal **T** and inversion **I** symmetries are broken simultaneously. As a consequence, ferroelectric polarization can be induced by the application of external magnetic field and vice versa. To date, ME materials are considered as platform to investigate several novel concepts, such as ME monopole or toroidal moment. Honeycomb-based materials have been attracting lots of attention owing to its fascinating physics as exemplified by the emergence of massless Dirac fermion and a spin liquid state. Although several theoretical works suggest the existence of several interesting phenomena accompanied with honeycomb magnet upon symmetry breaking, the physical response in term of ME coupling in this class of materials is not fully studied. The main purpose of this thesis is devoted to investigate ME response arising from honeycomb based magnets, which includes $Co_4A_2O_9$ (A = Nb, Ta) and zigzag antiferromagnetic spin chain $MnNb_2O_6$. Intriguing ME coupling found on these systems may shed a new light toward understanding mechanism of multiferroic and ME materials.

For the experimental study, single crystals were grown by floating zone method. Magnetization was determined using a superconducting quantum interference device. Dielectric constant was measured by using a LCR meter. Electric polarization as a function of temperature and magnetic field was calculated by integrating displacement current with time. Synchrotron X-ray measurements were performed on beam lines BL3A and 8A at Photon Factory, KEK, Japan. Magnetic structure was determined using a time-of-flight neutron diffractometer BL18 SENJU installed at MLF, PARC Japan.

$Co_4Nb_2O_9$ crystallizes in the trigonal structure (space group $P\text{-}3c1$) and undergoes an antiferromagnetic (AFM) phase transition at $T_N = 27.2$ K. The crystal structure can be viewed as alternating honeycomb layers consisting of hexagonal rings of CoO_6 octahedra stacked along trigonal axis. The buckled honeycomb network of Co^{2+} ions accompanied with strong spin-orbit coupling makes this material a promising candidate to explore interesting phenomena inherited from honeycomb structure. Single crystal neutron diffraction and magnetic susceptibility measurements reveals that magnetic structure is different from collinear $\text{-}3'm'$ with spin parallel to the trigonal axis as proposed by a previous study. Magnetic moments are found to be ordered almost in the basal plane, which can be described by magnetic space group $C2/c'$ with propagation vector $\boldsymbol{k} = 0$. Associated with magnetic phase transition, sharp anomalies in dielectric constant and displacement current indicate the emergence of ferroelectric polarization at T_N. The polarization exhibits linear dependence on external magnetic field up to 14 T, which reveals a large coupling constant of 30 ps/m. Detail measurement of ME coupling revealed that all the components in ME tensor are non-zero, which can be attributed to reduction of symmetry due to

the ordering of magnetic moment. The appearance of off-diagonal components in ME tensor of $Co_4Nb_2O_9$ implies the formation of ferrotoroidic order, which may give rise to intriguing phenomena, such as large directional dichroism or non-linear optical effect. More interestingly, we observe the continuous variation of polarization along $P_{[110]}$ direction under rotating magnetic field in-plane. As the magnetic field rotates clockwise by an angle θ, the polarization rotates counterclockwise by an angle twice larger -2θ. This intriguing effect may be attributed to the anti-symmetric deformation of band structure arising from the adjustment of spin configuration in honeycomb network under rotating magnetic field. Such a kind of unique ME response can be considered as a general feature for other honeycomb magnets accompanied with in-plane antiferromagnetic order. Finally, in $Co_4Nb_2O_9$, orbital angular momentum is not completely quenched because of strong spin-orbit coupling; orbital moments can contribute to the emergence of linear magnetoelectricity as proposed recently. The effect can be identified by examining the dependence of orbital angular momentum on external applied electric field.

Toward better understanding about ME response in honeycomb antiferromagnet, we investigate the magnetic and ME effect in analogous material, $Co_4Ta_2O_9$. The in-plane magnetic structure below Neel temperature T_N = 20 K can be confirmed via magnetic susceptibility measurement in single crystalline sample. Surprisingly, ME response measured in similar condition with $Co_4Nb_2O_9$ indicates non-linear ME response, which is closely related to a meta-magnetic phase transition observed in magnetization measurement. Determination of magnetic structure will be crucial to unveil the origin of this interesting ME response. Even though, the emergence of polarization in transverse configuration of magnetic field and electric field indicate the ferrotoroidic state, which can be the origin numerous intriguing effects as mentioned above.

Antiferromagnetic (AFM) order in zigzag chain can be considered as an odd-parity multiple order, which gives raise for several interesting effect such as ME coupling. Here we investigate zigzag AFM $MnNb_2O_6$ and find out that ME response in this material closely relates to magnetic toroidal order. Crystallized in orthorhombic structure *Pbcn*, $MnNb_2O_6$ exhibits antiferromagnetic order below T_N = 4.4 K. Accordingly, the ME effect can be realized simultaneously with the ordering of magnetic moment, which obeys the constraint of magnetic symmetry. Interestingly, application of magnetic field parallel spin direction $H \parallel a$ lead to the spin-flop phase transition at critical field H_C = 2.5 T. Comparing the ME response below and above H_C allows us to determine possible spin configurations above spin-flop phase transition. In any case, the existence of electric polarization under external magnetic field in antiferromagnetic phase can be explained in term of magnetic toroidal moment arising from zig-zag antiferromagnetic order in $MnNb_2O_6$. Finally, as magnetic field increases, dielectric constant accompanied with AFM order shifts toward lower temperatures. This interesting behavior suggests the possibility to observe Quantum critical end point or quantum critical point. In the latter case, $MnNb_2O_6$ can be considered as a unique platform to observe intriguing phenomena originating from a quantum state where different order parameters mutually coupled to each other.

In conclusion, we succeeded in growth single crystals of $Co_4Nb_2O_9$, $Co_4Ta_2O_9$ and $MnNb_2O_6$.

Detail investigation of magnetic and ME response revealed several intriguing properties. The results found on this study may be common features for other honeycomb antiferromagnetic materials.

論文審査の結果の要旨

Nguyen Duy Khanh（ヌイェン　ドゥイ　カーン）氏提出の博士論文「Magnetoelectric response in honeycomb antiferromagnets（ハニカム反強磁性体における電気磁気応答）」の研究目的は、ハニカム格子状に磁気モーメントが配列する反強磁性体における、新規電気磁気応答の探索とその微視的起源の解明である。氏が着目した $Co_4A_2O_9$ (A = Nb, Ta)は、粉末試料において電気磁気効果が報告されていたが、その報告の前からこの物質の可能性を見い出して単結晶育成に着手していた。育成した $Co_4Nb_2O_9$ 単結晶を用いて、中性子を用いた結晶構造解析及び磁気構造解析をおこなった。その結果、これまで、Co の持つ磁気モーメントが c 軸に平行に反強的に配列していると考えられていた磁気構造とは異なり、磁気モーメントが c 面内、即ちハニカム格子面に沿って配列しているという事を実験的に証明した。氏はこの単結晶を用いて、ハニカム格子面内に磁場を印加した場合に、電気分極が大きく誘起される事を世界で初めて発見した。更に磁場を面内で 90 度回転させた場合に電気分極が反転するという、新規の電気磁気応答も発見した。これらのマクロ現象とミクロ構造を結びつける微視的メカニズムについて検討し、これまで提唱されている磁気秩序誘起強誘電性のメカニズムでは得られた実験結果を説明できない事を明らかにした。氏は、空間反転と時間反転の両方の対称性が破れるトロイダルモーメントに着目し、その出現に伴って分裂するバンド構造の非対称性が、電気分極を生じると解釈し、新たな微視的起源を持つ強誘電性の可能性を提唱した。これまでの理論の枠組みでは存在し得なかった電気磁気効果を発見した事は、今後の実験理論物理の新たな展開を生む大きな原動力になる可能性がある。

氏の研究は、彼自身のアイデアから出発し、物質の選定、作成、実験、解析、解釈に至まで、全て氏自身が主体的に進めてきた研究である。この事は、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、Nguyen Duy Khanh（ヌイェン　ドゥイ　カーン）氏提出の博士論文は、博士（理学）の学位論文として合格と認める。