論文内容の要旨

論文題目: Excitonic Insulator Transition in the Zero-Gap Semiconductor Ta_2NiSe_5 (ゼロギャップ半導体 Ta_2NiSe_5 における励起子絶縁体転移)

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1. Introduction and objective

Excitonic insulator is an electronic phase theoretically predicted to be realized by hybridized gap formation associated with exciton condensation. It is expected to manifest itself in narrow-gap semiconductors and semimetals. In such low carrier density systems, Coulomb interaction between electron in conduction band and hole in valence band, E_B, is only weakly screened. When E_B exceeds the magnitude of band gap E_G, the system undergoes an excitonic insulator transition at T_c. In general, excitonic gap formation is accompanied by a periodic lattice distortion with periodicity of $2\pi/|\boldsymbol{q}|$ where $\boldsymbol{q}$ is wave vector connecting the conduction band minimum and the valence band maximum. T_c of excitonic insulator varies depending on the magnitude of E_G. T_c is maximized when E_G is zero, whereas it decreases away from the zero gap. T_c is suppressed as system becomes more insulating by increasing E_G. T_c is also suppressed when the valence and conduction bands are overlapped, namely in semimetals, since the increased number of carriers screens Coulomb interaction. Theoretically, the transition from semimetal-to-excitonic insulator can be described in the analogy of Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity while Bose-Eisnstein condensation (BEC) of exciton is predicted in the semiconductor region. Excitonic insulator therefore can be a solid-state platform to explore BCS-BEC crossover.

Despite such intriguing features, only a handful of candidates have been reported to date for excitonic insulator. 1*T*-$TiSe_2$ and Tm(Se, Te) are the well-known candidate materials. 1*T*-$TiSe_2$ undergoes a phase transition at 202 K and excitonic gap formation has been discussed from the angle-resolved

photoemission spectroscopy (ARPES). Tm(Se, Te) is a narrow gap semiconductor and proposed to display an excitonic insulator transition by applying pressure. Both of those are indirect gap systems and the phase transition is accompanied by the periodic lattice distortion. The strong lattice distortion complicates the electronic structure and hinders the exact evaluation of gap opening and the electronic entropy change associated with the transition. Alternative scenarios such as charge density wave and band Jahn-Teller effect have been also put forward to explain the phase transition especially in 1*T*-$TiSe_2$. In order to evidence the presence of excitonic insulator state, narrow gap semiconductor or semimetal with a direct gap ($\boldsymbol{q} = 0$) is highly demanded.

Recently, Ta_2NiSe_5 appeared as a prime candidate of excitonic insulator. Ta_2NiSe_5 crystalizes in a layered structure stacked by van der Waals interaction. Each layer of Ta_2NiSe_5 is composed by quasi-one dimensional chains of corner-shared $NiSe_4$ tetrahedra and edge-shared $TaSe_6$ octahedra. The band calculation indicates a finite direct gap at the Γ point ($\boldsymbol{q} = 0$) in Ta_2NiSe_5. The valence band is mainly composed by Ni 3*d* orbitals with Se 4*p* admixture while Ta 5*d* orbitals dominate the conduction band. Since the valence and conduction bands belong to the different irreducible representations, their hybridization is unexpected. This implies that Ta 5*d* orbitals are empty while Ni 3*d* and Se 4*p* orbitals are fully occupied. Reflecting the spatially-separated 1D chains without hybridization, both valence and conduction bands show strong 1D character. Ta_2NiSe_5 is reported to undergo a semiconductor-to-insulator transition at 328 K with absense of finite-$\boldsymbol{q}$ density wave formation. From the XPS measurement, it was suggested that Ta 5*d* and Ni 3*d* orbitals are partially hybridized below the transition. The gap opening with band flattening at the transition was also observed by ARPES. Based on these results, excitonic insulator transition was invoked in Ta_2NiSe_5.

In this study, we aimed to elucidate the excitonic insulator transition in Ta_2NiSe_5. To this end, it is indispensable to evaluate the excitonic gap opening and the entropy change associated with the transition. In an excitonic insulator, the hybridization gap opens in both valence and condution bands and a large entropy change is expected due to condensation of electrons and holes. Furthermore, the characteristic phase diagram should be a compelling evidence of excitonic insulator. In order to address these issues, we studied the transport, optical and thermodynamic properties, and demonstrated that the excitonic insulator transition takes place in Ta_2NiSe_5. Besides, by employing chemical doping and pressure, we controlled the band gap E_G and have drawn the predicted phase diagram.

2. Hybridized gap formation in Ta_2NiSe_5

Ta_2NiSe_5 is a narrow gap semiconductor and undergoes semiconductor-to-insulator transition at 326 K. The activation energy of the high temperature phase is estimated to be ~0.01 eV from the Arrhenius plot of resistivity. The in-plane resistivity is found to be anisotropic. The resistivity along the quasi-one dimensional chains (ρ_a) is more conductive than that perpendicular to the chains (ρ_c), which is consistent with the band structure. Below T_c, ρ_a increases significantly while ρ_c is less affected.

Consequently, this results in more isotropic in-plane resistivities at low temperatures. This implies a hybridized gap formation in the valance and conduction bands.

The hybridized gap formation is further evidenced by optical conductivity. At the lowest temperature 10 K, the magnitude of gap was found to be as large as 0.3 eV. Since the estimated activation energy above T_c is much smaller than 0.3 eV, this essentially corresponds to the magnitude of hybridized gap 2Δ. According to the previous ARPES study, the magnitude of gap was estimated to be 0.18 eV for the valence band. The 0.3 eV gap in the optical conductivity implies that the hybridized gap opens in both valence and conduction bands ($\Delta \sim 0.15$ eV for each), consistent with the excitonic insulator scenario. Considering T_c of 326 K, the transition is in the strong coupling regime with $2\Delta/k_BT_c = 12$.

The excitonic gap formation should make a significant change in the thermodynamic properties. In order to estimate the entropy change associated with the phase transition, we carried out heat capacity measurement. A pronounced anomaly can be identified at T_c. We estimated the lattice contribution to heat capacuty, $C_{lattice}$, by using the two-phonon Debye fit. The electronic contribution C_{el} was calculated by subtracting $C_{lattice}$. The result, plotted as C_{el}/T versus T, shows a clear jump at T_c and is reminiscent of a BCS-type superconducting transition, expected due to the formal analogy of the theories. The entropy change associated with the transition is estimated to be $\Delta S \sim 2$ J/(mol K) by integrating C_{el}/T as a function of temperature up to T_c. This magnitude corresponds to approximately 20 % of gas constant and clearly is too large to be accounted for only as phononic entropy change of the phase transition. The entropy change was satisfactory explained by considering the exciton condensation of electrons and holes in the range of ± 0.13 eV from the Fermi level. The energy range agrees with the gap obtained by optical conductivity. The data presented so far strongly suggest that excitonic insulator state is realized in Ta_2NiSe_5. Since Ta_2NiSe_5 is a semiconductor close to zero gap above T_c, it is expected to locate at the "optimal" point of the phase diagram. This gives us an opportunity to investigate the electronic phase diagram by driving the system towards more insulating and metallic regions.

3. Electronic phase diagram in Ta_2NiSe_5

Motivated by the zero gap feature of Ta_2NiSe_5, we investigated the electronic phase diagram by tuning the gap size. In order to increase the band gap, we employed sulfur substitution. Ta_2NiS_5 is known as an isostructural compound with Ta_2NiSe_5, and has larger activation energy of 0.17 eV. The band gap of Ta_2NiSe_5 is expected to be enhanced by sulfur substitution, and the system should enter the semiconducting side of phase diagram. Indeed, the activation energy of $Ta_2Ni(Se_{1-x}S_x)_5$ are found to be enhanced systematically as a function of sulfur content, x. When the gap increases, T_c is found to be suppressed. For sulfur doping larger than $x = 0.55$, no phase transition is observed down to 2 K. The phase diagram of semimetallic side was investigated by tellurium doping. We synthesized $Ta_2Ni(Se_{1-x}Te_x)_5$ in the range of $0 \le x \le 0.2$, and $Ta_2Ni(Se_{1-x}Te_x)_5$ with higher tellurium content was not successfully synthesized possibly due to solubility limit. The resistivity of Te-doped Ta_2NiSe_5 shows that

the T_c is again suppressed as the system becomes more conductive. In the chemical doping study, we found that both increase and decrease of activation energy suppress T_c.

Since semimetallic end point of the phase diagram was not accessible by tellurium doping effect, we carried out pressure experiments on undoped Ta_2NiSe_5, which is expected to make the system semimetallic. T_c indeed decreases by applying pressure as the phase transition is observed at 293 K with P = 1.8 GPa, much lower than 326 K of the ambient pressure. T_c is further lowered by increasing pressure, but the end point of the phase transition in the semimetallic region is not reached since the transition suddenly becomes unclear above $P \sim 3$ GPa. The resistivity value at 300 K decreases systematically by pressure, but suddenly increases around 3 GPa. This implies that another phase transition is induced by pressure and the excitonic insulator phase is displaced. The pressure-induced phase transition was found to occur also in tellurium and sulfur doped Ta_2NiSe_5 at the same pressure range. The fact that the transition takes place at the similar pressure with irrespective of the band gap and T_c implies that it is not associated with excitonic insulator transition, but rooted in the structural origin. Overall, both sulfur substitution and pressure are found to suppress T_c in Ta_2NiSe_5. Since Ta_2NiSe_5 is expected to be located in the optimal point with zero gap, these results are consistent with theoretical prediction of excitonic insulator.

4. Summary

Ta_2NiSe_5 is to date the sole candidate of excitionic insulator with a direct gap, and we investigated the its transport, optical conductivity and thermodynamic properties. The data presented here is the key evidences for the existence of an excitonic insulator phase below T_c. In particular the thermodynamics of the phase transition is dominated by the excitation gap Δ opening between the conduction and valence band in this direct gap semimetal. The optical data is the first direct spectroscopic measurement of this many-body gap as a function of temperature. Intriguingly the observed gap is in very good agreement with the basic theoretical estimates of the exciton binding energy in this compound. Furthermore, the electronic phase diagram of Ta_2NiSe_5 well reproduces the theoretical prediction. We therefore argue that a zero-gap semiconductor Ta_2NiSe_5 exhibits the long-sought excitonic insulator transition.