

Pressure induced insulator to metal transition in quantum spin liquid candidate $NaYbS_2$

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Pressure induced insulator to metal transition in quantum spin liquid candidate $NaYbS_2$

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Pressure induced insulator to metal transition followed by the appearance of superconductivity has been observed recently in inorganic quantum spin liquid candidate $NaYbSe_2$. In this paper, we study the properties of isostructural compound $NaYbS_2$ under pressure. It is found that the resistance of $NaYbS_2$ single crystal exhibits an insulating state below 82.9 GPa, but with a drop of more than six orders of magnitude at room temperature. Then a minimum of resistance is observed at about 100.1 GPa and it moves to lower temperature with further compression. Finally, a metallic state in the whole temperature range is observed at about 130.3 GPa accompanied by a non-Fermi liquid behavior below 100 K. The insulator to metal transition, non-monotonic resistance feature and non-Fermi liquid behavior of $NaYbS_2$ under pressure are similar to those of $NaYbSe_2$, suggesting that these phenomena might be the universal properties in NaLnCh_2 (Ln = rare earth, Ch = O, S, Se) system.

Keywords: high pressure, quantum spin liquid, insulator to metal transition, $NaYbS_2$

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1. Introduction

Quantum spin liquid (QSL) is an exotic quantum ground state in condensate matter physics, which shows no long-range magnetic order even at absolute zero temperature due to the strong quantum fluctuation.[1–3] The features of long-range quantum entanglement and fractionalized excitations for quantum spin liquid have great potential applications in quantum communication and quantum computation.[2] More importantly, P. W. Anderson proposed that quantum spin liquid is the ground state of high temperature superconductivity (HTSC), and superconductivity could be realized through insulator to metal transition (MIT) of QSL.[4] Thus, tremendous efforts have been devoted to investigating the Mott transition of QSL.[5–8] However, most of the attempts failed owing to the high energy gap or the difficulty of inducing enough charge carriers doping in the inorganic quantum spin liquid system.

Recently we observed pressure induced MIT followed by the appearance of superconductivity in the inorganic quantum spin liquid candidate $NaYbSe_2$.[9] $NaYbSe_2$ belongs to the NaLnCh_2 (Ln = rare earth, Ch = O, S, Se) system, which has been proposed to be a promising candidate to realize QSL state.[10–14] Around these compounds, $NaYbSe_2$ possesses the smallest energy gap (1.9 eV), showing great potential to be a metallic state under pressure. This is the first observation of the Mott transition and superconductivity in an inorganic quantum spin liquid system, and can avoid the mess of disorder like that in organic QSL and makes it a good choice to investigate the intrinsic properties of QSL. Recently, Yang *et al.* explored the underlying mechanism of the insulator-to-metal transition and superconductivity of $NaYbSe_2$ and established an overall picture of its electronic phases under pressure utilizing density functional theory and the dynamical mean-field theory.[15] They found the superconductivity emerged in the heavy fermion phase with well-nested Yb-4f Fermi surfaces, suggesting that spin fluctuations may play a role in the Cooper pairing. Moreover, they pointed out that $NaYbSe_2$ might be the third Yb-based heavy-fermion superconductor with a very high T_c than most heavy fermion superconductors.

$NaYbS_2$ is isostructural to $NaYbSe_2$, and possesses the second smallest energy gap (2.7 eV) in this NaLnCh_2 (Ln = rare earth, Ch = O, S, Se) series compounds.[11] To have a deep insight into the intrinsic physics properties of this series of compounds especially the Mott transition and superconduc-

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tivity, in this paper, we systematically investigate the high-pressure transport properties of $NaYbS_2$ single crystal and the crystal structure evolution up to 150 GPa.

2. Experiment

$NaYbS_2$ single crystals were grown by flux method. The Yb powder, S powder and NaCl grain (as flux and Na source) were mixed together with the molar ratio of 2:3:10 and loaded into a silica tube and then sealed under Ar atmosphere ($\sim$ 0.2 atm). The sealed tube was heated to 900 °C–950 °C for 24 h and kept at that temperature for 150 h, and cooled down to room temperature. Finally, the single crystals were got after washing NaCl flux using distilled water several times.[11]

Transport properties of $NaYbS_2$ under high pressure and low temperatures were measured through Van der Pauw method using a diamond anvil cell (DAC) made of CuBe alloy.[16–19] A pair of diamonds with a 100 μm diameter culet were used to generate pressure. A T301 stainless steel gasket was pressed from a thickness of 250 μm to 20 μm, and drilled a center hole with a diameter of 300 μm. The gasket was covered by cubic boron nitride (cBN) powder to protect the electrode leads insulated from the metallic gasket. The sample chamber was a 100 μm-diameter center hole in the insulating layer and the pressure transmitting medium was NaCl powder. The sample size was about 40 μm × 40 μm × 5 μm. The electrodes were slim Au wires with a diameter of 18 μm. The pressure was measured via the ruby fluorescence[20] and Raman spectra of the diamond anvil were adopted to calibrate pressure for the experiments above 100 GPa. The diamond anvil cell with samples and electrodes was loaded inside a cooled cryostat system to perform the experiments. A thermometer was mounted near the diamond in the diamond anvil cell to monitor the exact sample temperature. Raman spectra measurement was performed using the Renishaw micro-Raman spectrometer with a symmetric Mao–Bell DAC at room temperature. The wavelength of laser was 532 nm.

3. Results and discussion

Figure 1 shows the temperature dependence of resistance of $NaYbS_2$ single crystals in the *ab*-plane. It can be seen clearly that below 15.9 GPa, the sample shows a very high insulating property, even out of the range of the measurement. Under higher pressure, the resistance decreases quickly but still keeps an insulting state below 82.9 GPa. The absolute values of resistance at room temperature decrease with increasing pressure dramatically by more than six orders of magnitude. This behavior is similar to that $NaYbSe_2$, but with a much smaller rate. The decreasing rate for $NaYbSe_2$ is about 0.3 orders of magnitude per GPa, while the corresponding value for $NaYbS_2$ is about 0.12. This result indicates that $NaYbS_2$ shows more insulting behavior than that $NaYbSe_2$, which is coincided with the truth that energy gap of $NaYbS_2$ (2.7 eV) is larger than that $NaYbSe_2$ (1.9 eV). Under further compression, a metallic state emerges at 100.1 GPa, but with a minimum resistance at about 80 K (named T_{min}). The temperature for the T_{min} moves to a lower temperature and finally almost disappears at about 122.8 GPa. The upturn behavior of resistance below T_{min} obeys the rules of logarithmic temperature dependence and is recognized as a weak localization area as that in $NaYbSe_2$.[9] Yang *et al.*' DFT calculation indicated that the resistance should be dominated by incoherent Kondo scattering.[15] Here, we find both $NaYbS_2$ and $NaYbSe_2$ show similar behavior, suggesting that it may be the intrinsic physical property related to the 4f electron.

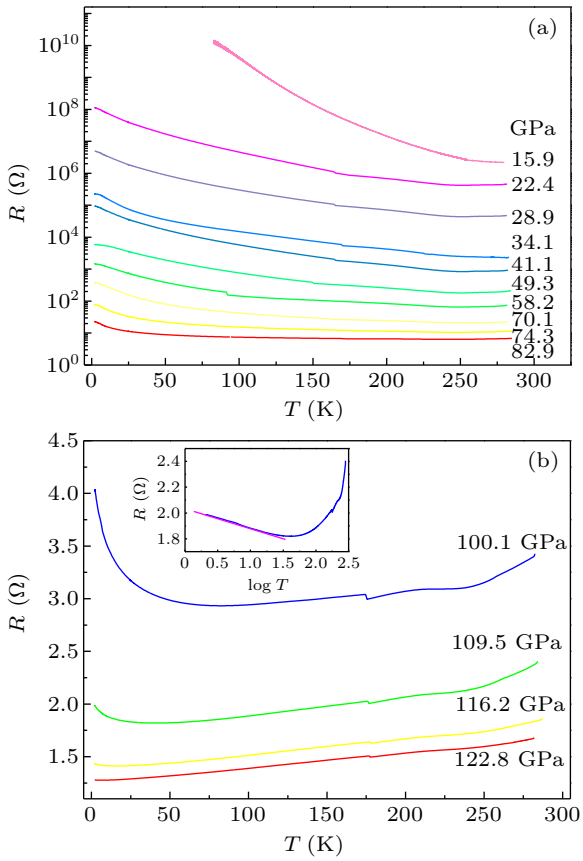


Fig. 1. Pressure effect on the resistance of $NaYbS_2$. (a) Temperature dependent resistance for $NaYbS_2$ single crystal in insulating state up to 82.9 GPa. (b) Temperature dependence of resistance of $NaYbS_2$ single crystal between 100.1 GPa and 122.8 GPa. The inset shows the resistance vs. log T data at 109.5 GPa, showing a linear behavior below T_{min} (see magenta line).

The piezochromism of the $NaYbS_2$ single crystal also coincides with that transport properties, reflecting the narrowing of the band gap. The color of $NaYbS_2$ single crystal is light blue at 3.1 GPa, which is coincided with the result reported in previous work.[11] It becomes deep blue at about 22.4 GPa, and then becomes red at 41.4 GPa. When the pressure was enhanced up to 58.2 GPa, there is only a small amount of red color can be seen, indicating the gradual decrease of band gap. The sample becomes completely dark when pressure is above

74.3 GPa. However, the sample is still in an insulating state, indicating the band gap is very small but still not completely closed.

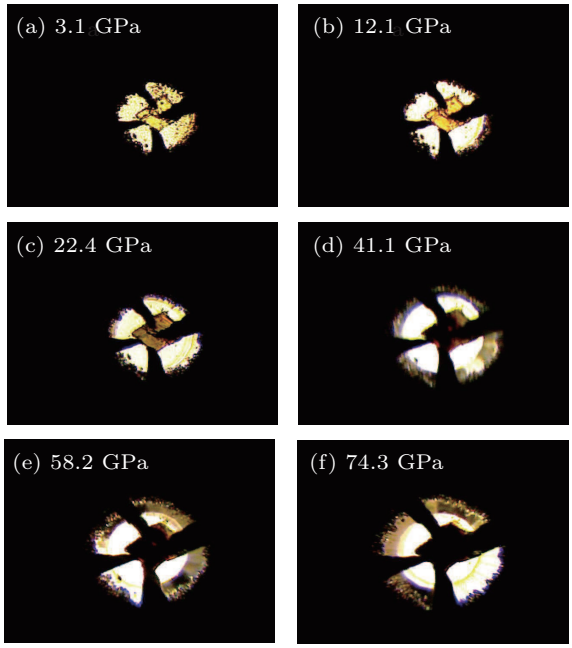


Fig. 2. Pressure dependent piezochromism of the $NaYbS_2$ single crystal.

$NaYbS_2$ single crystal becomes completely metallic at about 130.3 GPa (see Fig. 3). Moreover, it is noted that the metallic state at low temperature range shows a nearly linear behavior, indicating a non-Fermi liquid behavior. We have applied the power-law fitting $R(T) = R_0 + AT^n$ to the resistance of $NaYbS_2$ at 130.3 GPa and 140.6 GPa, respectively. The orange line in Fig. 3 shows the fitting result of $R(T)$ between 8 K and 100 K at 140.6 GPa. It can be seen that the power-law formula fits the experimental data well in this temperature range. The pressure dependence of the exponent n is about 1.01 and 0.98 respectively, clearly indicating a non-Fermi liquid behavior, and it is also similar to $NaYbSe_2$. However, superconductivity is absent in the whole pressure range of our experiment. We believe it may need higher pressure to drive a non-Fermi liquid behavior to Fermi liquid one and finally the emergence of superconductivity.

Next, we focus on the structural evolution of $NaYbS_2$ under pressure. Pressure dependent Raman spectra for $NaYbS_2$ single crystal are shown in Fig. 4. There are four obvious vibration modes at around 196 cm^{-1}, 260 cm^{-1}, 286 cm^{-1} and 576 cm^{-1}, assigned as modes 1, 2, 3 and 4, respectively. We use the Gaussian function to fit the peak position of the Raman spectrum. It can be seen clearly that with the increase of pressure the Raman vibration modes shift to the high frequency (Fig. 4(a)), indicating the contraction of sample. There is a new vibration mode that appeared at 13.5 GPa at 224 cm^{-1} (see asterisk in Fig. 4(a), assigned as mode 5), signifying the phase transition occurring (see Fig. 4(b)). The transition pressure (13.5 GPa) is higher than that $NaYbSe_2$ (11 GPa). The details of crystal structure evolution still need to be further investigated using the high-pressure x-ray diffraction.

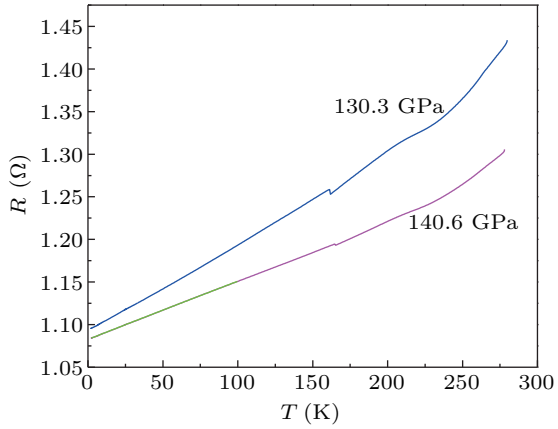


Fig. 3. Temperature dependence of $R(T)$ for $NaYbS_2$ single crystal in metallic state at 130.3 GPa and 140.6 GPa. The green line demonstrates the experimental fitting results of $R(T)$ below 100 K at $P = 130.6$ GPa using the formula $R(T) = R_0 + AT^n$.

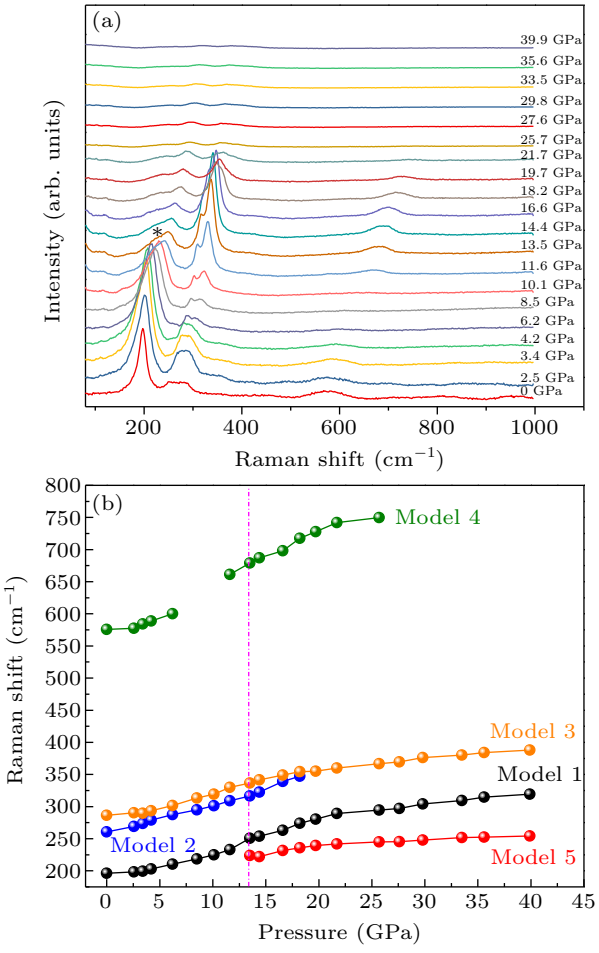


Fig. 4. (a) Raman spectrum at selected pressures at room temperature for $NaYbS_2$. The asterisk indicates a new vibration mode. (b) Evolutions of Raman vibration modes as functions of pressures for $NaYbS_2$.

From the above results, it can be clearly seen that both $NaYbSe_2$ and $NaYbS_2$ show similar behaviors, including the MIT, minimum of resistance and non-Fermi liquid behavior at high pressure region, suggesting they might be universal for $NaLnCh_2$ system at high pressure and low temperature

region. Moreover, the $NaLuSe_2$, which shows almost same crystal structure as $NaYbSe_2$ and $NaYbS_2$, does not show any MIT behavior around 100 GPa (the result will be published elsewhere). Noted that the Lu^{3+} ion possesses a $4f^{14}$ electron configuration, which means that the f orbital is fully occupied and the 4f electrons should have no attribution to the transport properties. This result further confirms the important role of 4f electron in this system and coincides with Yang *et al.*'s result.[15]

Though the rich diversity of the family members of $NaLnCh_2$ allows tunable charge gaps, variable exchange coupling, and many other advantages, and makes this family as an ideal platform for fundamental research of QSLs and its promising applications, most of them show a very high insulting state. This property makes it very difficult to accurately control the pressure to get the quantum critical point from the insulating state to the metallic state and finally to superconductivity. Thus, it is very difficult to establish an accurate relationship between QSL and SC. As to this 4f-electron system, it also will be very difficult to confirm the existence of new heavy fermion superconductor using the specific heat under such high pressure. Thus, the discovery of new QSL materials which can realize the Mott transition in a much lower pressure or even ambient pressure is still a challenge.

4. Conclusion

We investigate the high-pressure transport and structure evolution of inorganic QSL candidate $NaYbS_2$ single crystal. An MIT appears at around 58.9 GPa and the metallic state in the whole temperature range is observed at around 122.8 GPa. High pressure Raman measurements demonstrate that there is a structural phase transition around 26.8 GPa. The decrease rate of resistance and the applied pressure for the appearance of metallic states in $NbYbS_2$ are much higher than that $NaYbSe_2$, coinciding with the higher insulating behavior of $NaYbS_2$ than that of $NaYbSe_2$.

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