Exciton transport in the electron-hole system Ta_2NiSe_5

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We have measured the dielectric constant and thermopower of single crystal samples of the excitonic insulator candidate Ta_2NiSe_5. The dielectric constant below 50 K shows relaxor-like relaxation, implying the existence of randomly distributed electric dipoles. We have evaluated the concentration of the dipoles to be 10^{19} cm^{-3} at 30 K, which gives a rough estimate of the exciton concentration in this compound. A large thermopower of 600 μV/K at 100 K suddenly drops toward zero down to 50 K, and this zero thermopower evidences the neutral particles flow against the applied temperature gradient. We have semi-quantitatively explained the above two anomalies in terms of spontaneously generated excitons at low temperatures where thermally excited holes are quenched.

Exploration of a novel quantum state such as unconventional superconductivity and topologically nontrivial states in exotic materials has been a central issue in the modern condensed matter physics. In this viewpoint, the excitonic insulator (EI) phase, the ideas for which were proposed in the 1960's [1-6] , deserves to be explored as an unconfirmed quantum state. In the EI phase, a macroscopic number of excitons, which are tightly-bound electron-hole pairs, are spontaneously generated and condensed into a single quantum state. Unfortunately, the EI phase has not yet been detected experimentally owing to lack of model compounds.

A ternary transition metal chalcogenide, Ta_2NiSe_5 [7] has been recently proposed as a candidate of the EI. An extremely flattened band dispersion in a single particle excitation spectrum observed by an angle resolved photoemission spectroscopy [8] is regarded as evidence of the EI phase in this compound. Theoretical calculation has also confirmed its excitonic instability coupled with a structural phase transition from orthorhombic to monoclinic at 328 K [9-11] by using the three-chain Hubbard model [12]. Furthermore, since Ta_2NiSe_5 is insulating, it is more appropriate than other candidates. For instance, SmS under high pressures [13] and 1*T*-$TiSe_2$ [14][15] have metallic ground states which may screen exciton contribution. Thus we believe that Ta_2NiSe_5 is an ideal platform to answer to a long-standing problem whether or not a condensed state of excitons exists.

In spite of such great promise, there is no direct evidence for spontaneously generated electron-hole pairs in Ta_2NiSe_5. Although the dc resistivity measured by Lu et al. [16] is qualitatively consistent with a hypothetical phase diagram of the EI, it did not directly probe the dynamics of electron-hole pairs that are electrically neutral and

thereby do not feel dc field. Here we show the dielectric constant and thermopower of single crystals of Ta_2NiSe_5. The dielectric constant characterizes the charge response upon an ac field that rocks an electron-hole pair. In particular, when the electron-hole pairs are tightly bound, they can behave as permanent electric dipoles and should exhibit a peculiar ac response. Similarly a temperature gradient couples to excitons and thus, the net thermopower of an excitonic insulator should be expressed by superposition of thermally excited careers and excitons. Here we demonstrate that the both quantities are measured to be highly unconventional in Ta_2NiSe_5 at low temperatures, and we ascribe them to exciton transport.

Single crystals of Ta_2NiSe_5 were synthesized by the chemical vapor transport method. Stoichiometric amounts of element powders of tantalum, nickel and selenium were mixed and sealed into an evacuated quartz tube with a small amount of I_2 as a transport agent. The mixture was sintered under a temperature gradient of 900/780 ℃ for 1 week. Thin and platy crystals were obtained at low temperature side of the tube with a typical size of 10 × 1 × 0.1 mm^3. In order to confirm quality of the sample, the electrical resistivity was measured by the four-probe technique by using a PPMS(Quantum Design). The thermopower was measured with a steady state and the two-probe technique from 4 to 350 K by using the PPMS. The sample bridged two separated copper heat baths, and the resistance heater created a temperature difference between the two heat baths, which was monitored through a cooper-constantan differential thermocouple. The contribution of the voltage leads was meticulously subtracted. The dielectric constant was measured by using the two-probe technique with a homemade measurement station in a liquid He cryostat using an LCR meter (Agilent 4284A). The measurement temperature range was from 4 to 300 K with frequencies of 100, 1 k, 10 k, 100 k and 1 MHz.

Figure 1 shows the temperature dependence of the resistivity along the *a*, *b* and *c* axes. It should be noted that the resistivity along the *b* axis was obtained from the imaginary part of the dielectric constant at 100 Hz. Since Ta_2NiSe_5 has characteristic Ta and Ni quasi-one- dimensional chains, the *a* axis electric resistivity is less insulating than that measured at 300 K along the other two axes. In contrast, the resistivity becomes less anisotropic below 100 K. There is a tiny kink along the *a* axis at 330 K which indicates the phase transition temperature T_s. In addition, humps are observed along the *a*, and *c* axes below 100 K. Such trends are consistent with those reported in a previous study [16].

The existence of localized electron-hole pairs are most clearly seen in their dielectric response. Figure 2 (a) shows the temperature dependence of the dielectric constant ε along the *b* axis (cross-plane) direction. This is because the *b* axis dielectric constant is most accurately measured because of the highest resistivity and the thinnest dimension [17]. The dielectric constant at 80 K is as huge as 10^4 at 1 kHz, and rapidly decreases down to 60 K. Such behavior is due to free carriers thermally activated at high temperatures.

As the temperature decreases below ~50 K, the dielectric constant shows an anomalous plateau above a frequency-dependent temperature T_{max}. The dielectric constant finally shows a frequency-independent value of 22 below 15 K, which is consistent with the value evaluated from the optical conductivity along the *a* axis [18]. Using the dielectric constant at the lowest temperature we can evaluate an exciton Bohr radius $a_{exciton}$ as $a_{exciton} = 13.6 a_B E_B \varepsilon_0 / \varepsilon$, where a_B is the Bohr radius, and E_B is the binding energy of excitons. If we assume E_B to be ~0.1 eV, we estimate $a_{exciton}$ to be ~3 Å. It is noteworthy that the broad dielectric anomaly was intrinsic and well reproduced regardless of the species of electrodes and the amplitude of external field.

In order to clearly show the anomaly at T_{max}, high temperature contribution was carefully subtracted as shown by the solid curve in Fig. 2(a). The resultant contribution takes a broad maximum at T_{max} which varies with frequency as shown in Fig. 2(b). This behavior is reminiscent of relaxor ferroelectrics in which polar nano regions freely fluctuating at high temperatures gradually freeze with decreasing temperatures [19] [20].

Here we discuss the origin of the dielectric response of Ta_2NiSe_5. Similarly to the relaxor ferroelectrics, T_{max} obeys the Vogel-Fulcher law $f = f_0 \exp[-E_0 / k_B(T_{max} - T_f)]$, where T_f is a glass-forming temperature [21]. Figure 2 (c) shows the measurement frequencies as a function of $1/(T_{max} - T_f)$, and clearly indicates the validity of the Vogel-Fulcher law from which f_0, T_f, and E_0/k_B are evaluated to be 5×10^7 Hz, 23 K, 112 K, respectively. Thus we conclude that the dielectric relaxation in Fig. 2(b) evidences the existence of disordered arrangements of the electric dipoles.

We notice that however, Ta_2NiSe_5 does not exhibit a ferroelectric phase transition until 30 K[10] and, thus this ferroelectric behavior comes from an electronic origin. Actually the value of f_0 is too small for relaxor ferroelectrics, but can rather associate this with f_0 in the dielectric relaxation of the spin liquid candidate κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ [22]. In this particular organic salt, the dimerized BEDT-TTF molecules form a triangular square lattice, and the hole fluctuates within each dimer, which can be regarded as “dipole liquid” --an example of electronic ferroelectricity. This picture is highly consistent with the ac response of tightly-bound electron-hole pairs in the title compound.

Following the discussion in [22], we evaluate the number of electric dipoles. The red broken line in Fig. 2 (c) represents Curie-Weiss fitting from which the Curie constant and the Curie-Weiss temperature are evaluated to be 1×10^3 and 28 K, respectively. In the model of the order-disorder transition, the number of electric dipoles is expressed as $N = \varepsilon_0 k_B C / p^2$, where p is an electric dipole moment expressed by $p = ex$, where x is the electron-hole distance. If we assume x to be 3 Å ---the distance between the Ta and Ni chains, we estimate N to be 10^{19} cm^{-3}. Since the carrier density estimated from Hall measurement is approximately 10^{21} cm^{-3} at 300 K [16], the exciton concentration contributing to low-temperature electric dipoles is of the order of 1% of the carrier concentration at room temperature. This rough estimation is consistent with previous studies of the thermodynamics [16] and

theoretical calculations [12].

Low-temperature thermopower further consolidates the evidence for spontaneously generated excitons. Figure 3(a) shows the temperature dependence of the thermopower of Ta_2NiSe_5 along the *a* and *c* axes. The two pieces of the single crystals were cut out from one single crystal. At 350 K, the sign of the thermopower is positive along both the *a* and *c* axes, indicating that holes are the majority carrier. As temperature decreases from 350 K, the thermopower along the *a* axis shows no anomaly at T_s, then increases above 600 μV/K at 100 K. Figure 3(b) shows the thermopower plotted as a function of inverse temperature $1/T$. Since the thermopower increases linearly from 0.004 to 0.006 K^{-1}, an intrinsic semiconductor model [23] given by $\alpha = E_g/2qT + \alpha_0$ fits well over this temperature range, where q is the electric charge, E_g is the band gap and α_0 is the thermopower in the high-temperature limit. From the fitting, E_g was estimated to be 0.12 eV at 100 K, which agreed well with an optical gap of 0.16 eV[16]. The thermopower along the *c* axis direction also increases with decreasing temperature, although the temperature dependence is qualitatively different from the *a* axis direction.

The most striking feature is that the thermopower drops to a small constant value below 100 K. Such temperature dependence is highly incompatible with the intrinsic semiconductor model. It is noteworthy that this thermopower anomaly seems to be accompanied with the hump of the resistivity below 100 K, where the exciton contribution becomes gradually evident. Unfortunately we failed in measuring the thermopower below 50 K because of the high sample resistance.

We emphasize that the “zero” thermopower is another piece of evidence for the existence of excitons. Since the exciton is a tightly-bound electron-hole pair, the temperature gradient acts as an external force to move the pair from the high to low temperature side. When the pairs carry heat much more than the thermally excited holes, the pairs dominate transport where electrical currents of the electrons and holes cancel each other to give zero thermopower. If the pair were completely localized, it would carry neither heat nor electricity, and the thermopower would continue to show $1/T$ behavior at lower temperatures. We already evaluated the exciton concentration is of the order of 1% of the hole concentration at 300 K, and naturally expect that the exciton transport will dominate at such low temperatures where the thermally excited hole decreases below 1% from the room temperature value.

The spontaneously generated excitons have been sought near T_s in this compound. The present study indicates, however, that their transport is evident only below 100 K, far below T_s, since overwhelming contribution of thermally excited holes smears and screens the exciton contribution at higher temperatures. Since there is no thermodynamic anomaly other than T_s, low-temperature transport has been overlooked thus far. We should also note that we have not yet detect the quantum condensation. Low-temperature experiments including phase-sensitive measurements are necessary to step further.

In conclusion, we have measured dielectric constant and thermopower of Ta_2NiSe_5 single crystals. The relaxor-like dielectric response has been detected along the *b* axis direction below 50 K, indicating that excitons act as randomly distributed electric dipoles. Anomalous drops of the thermopower below 100 K has been observed, evidencing a crossover from the conventional charge transport of thermally excited careers to exciton transport. The present results indicate that the excitons dominate low-temperature transport in Ta_2NiSe_5, and support recent experiments and theories which have suggested a strongly coupled excitonic phase realizes in Ta_2NiSe_5 [24] [25]. We emphasize that the relaxor-like dielectrics accompanied by the zero-thermopower characterizes the title compound, and never been seen in any other materials. We propose that the dielectric constant and thermopower measurements are the powerful tools for exploring excitonic insulators.

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[1] L. V. Keldysh, and Y. V. Kopeav, Sov. Phys. Solid State **6**, 2219 (1965).

[2] J. Des Cloizeaux, J. Phys. Chem. Solids **26**, 259 (1965).

[3] D. Jérome, T. M. Rice, and W. Kohn, Phys. Rev. **158**, 462 (1967).

[4] W. Kohn, Phys. Rev. Lett. **19**, 439 (1967).

[5] B. I. Halperin, and T. M. Rice, Rev. Mod. Phys. **40**, 755 (1968).

[6] B. I. Halperin, and T. M. Rice, Solid State Physics, Vol. 21 (Academic Press, New York, 1968) p. 115.

[7] S. A. Sunshine, and J. A. Ibers, Inorg. Chem. **24**, 3611 (1985).

[8] Y. Wakisaka, T. Sudayama, K. Takubo, T. Mizokawa, M. Arita, H. Namatame, M. Taniguchi, N. Katayama, M. Nohara, and H. Takagi, Phys. Rev. Lett. **103**, 026402 (2009).

[9] F. J. DiSalvo, C. H. Chen, R. M. Fleming, J. V. Waszczak, R. G. Dunn, S. A. Sunshine, and J. A. Ibers, J. Less-Common Met. **116**, 51 (1986).

[10] A. Nakano, T. Hasegawa, S. Tamura, N. Katayama, S. Tsutsusi, and H. Sawa, Phys. Rev. B, **98**, 045139 (2018).

[11] A. Nakano, K. Sugawara, S. Tamura, N. Katayama, K. Matsubayashi, T. Okada, Y. Uwatoko, K. Munakata, A. Nakao, H. Sagayama, R. Kumai, K. Sugimoto, N. Maejima, A. Machida, T. Watanuki, and H. Sawa, IUCrJ, **5,** 158 (2018).

[12] T. Kaneko, T. Toriyama, T. Konishi, and Y. Ohta, Phys. Rev. B **87**, 035121 (2013).

[13] K. Matusbayashi, K. Imura, H. S. Suzuki, G. Chen, N. Mori, T. Nishioka, K. Deguchi, and N. K. Sato, J. Phys. Soc. Jpn. **76**, 033602 (2007).

[14] F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak, Phys. Rev. B **14**, 4321 (1976).

[15] Th. Pillo, J. Hayoz, H. Berger, F. Lévy, L. Schlapbach, and P. Aebi, Phys. Rev. B **61**, 16213 (2000).

[16] Y. F. Lu, H. Kono, T. I. Larkin, A. W. Rost, T. Takayama, A. V. Boris, B. Keimer, and H. Takagi, Nat. Commun. **8**, 14408 (2017).

[17] T. Takayanagi, M. Kogure, and I. Terasaki, J. Phys.: Condens. Matter **14**, 1361 (2002).

[18] T. I. Larkin, A. N. Yaresko, D. Pröpper, K. A. Kikoin, Y. F. Lu, T. Takayama, Y. –L. Mathis, A. W. Rost, H. Takagi, B. Keimer, and A. V. Boris, Phys. Rev. B **95**, 195144 (2017).

[19] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttg, J. Appl. Phys. **68**, 2916 (1990).

[20] A. Bokov, and Z.-G. Ye, J. Mater. Sci. **41**, 31 (2006).

[21] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttg, J. Appl. Phys. **68**, 2916 (1990).

[22] M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, Phys. Rev. B **82**, 125119 (2010).

[23] H. Goldsmid, and J. Sharp, J. Electr. Mater., **28**, 869 (1999).

[24] K. Seki, Y. Wakisaka, T. Kaneko, T. Toriyama, T. Konishi, T. Sudayama, N. L. Saini, M. Arita, H. Namatame, M. Taniguchi, N. Katayama, M. Nohara, H. Takagi, T. Mizokawa, and Y. Ohta, Phys. Rev. B **90**, 155116 (2014).

[25] K. Sugimoto, S. Nishimoto, T. Kaneko, and Y. Ohta, Phys. Rev. Lett. **120**, 247602 (2018).

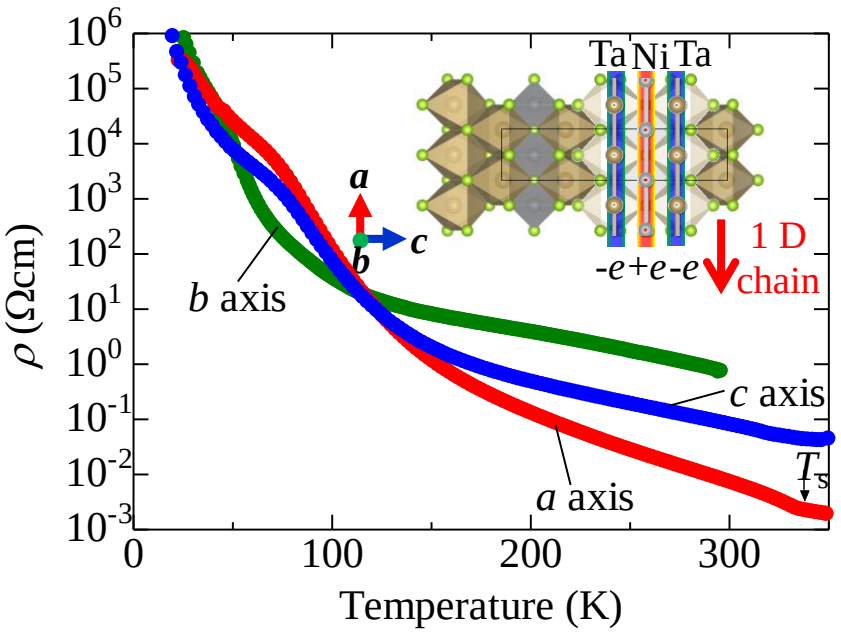

Figure 1 Resistivity of Ta_2NiSe_5 using single crystals. Red, green and blue plots show the resistivity along the *a*, *b* and *c* axes, respectively. Schematic crystal structure of Ta_2NiSe_5 is also displayed in the inset.

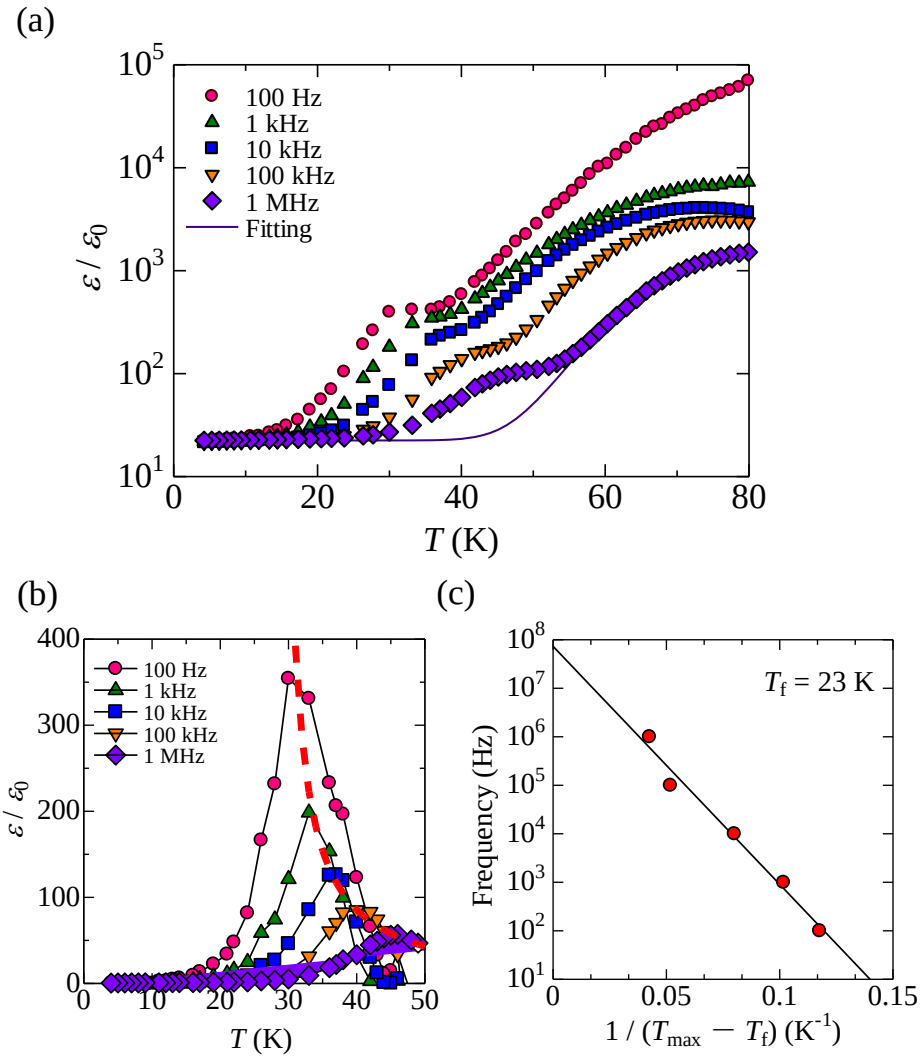

Figure 2 (a) The dielectric constant of a single crystal of Ta_2NiSe_5 along the *b* axis (cross-plane). (b) The residual curve by subtracting the high-temperature contribution from Fig. 2 (a). The red broken curve shows the Curie-Weiss fitting, where C and T_c are evaluated to be 1×10^3 and 28 K, respectively. (c) The measurement frequencies f are plotted as a function of $1 / (T_{max} - T_f)$. T_{max} is the temperature at which the dielectric constant goes through a broad maximum, and T_f is assumed to be 23 K. The solid line corresponds to the fitting curve, where f_0, and E_0 / k_B are evaluated to be 5×10^7 Hz, and 112 K, respectively.

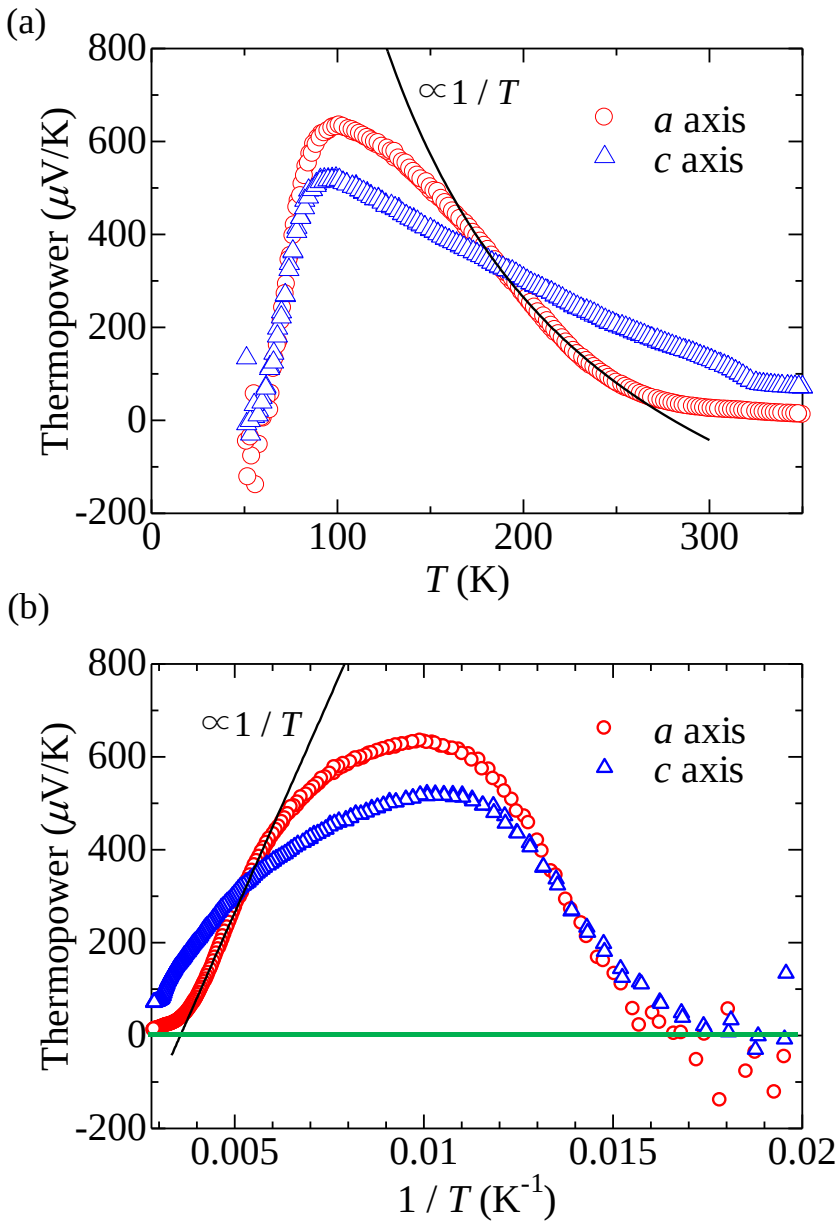

Figure 3 The thermopower of single crystals of Ta_2NiSe_5 plotted as a function of (a) temperature (b) inverse temperature along the *a* and *c* axes. Drastic drops of the thermopower take place below 100 K.