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# Anomalous thermopower in the organic compound $\theta$-(BEDT-TTF)$_2$Rb$M$(SCN)$_4$ ($M$=Zn,Co)

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We have investigated the thermopower in the organic compound $\theta$-(BEDT-TTF)$_2$Rb$M$(SCN)$_4$ ($M$=Zn,Co) in both its normal and rapidly cooled states. The anomalous temperature dependence of the thermopower is found to extend into the rapidly cooled state and reveals that the charge carriers exhibit both localized and itinerant behaviors. We propose a simple model that captures this feature on the basis of an extended Hubbard model.

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## INTROUCTION

Ever since the discovery of the high-$T_c$ superconductors,[1] the study of highly correlated systems has intensified in the hope of finding more exotic states with anomalous physical properties. The "spin liquid" state found in NiGa$_2$S$_4$,[2] $\kappa$-(BEDT−TTF)$_2$Cu$_2$(CN)$_3$ (Ref. 3) and the ultraclean carbon nanotubes[4] is an example of such states. In analogy to the "spin-liquid" state, the melting of charge ordering in frustrated lattice into a metallic state has also attracted much attention recently.[5] The $\theta$-type organic compounds are an ideal system to study such a melting in a quarter-filled hole system as the electronic correlation parameters $U/t$ and $V/t$ can be tuned.[6,7] This tuning is achieved by changing the dihedral angle ($\theta$) (see Fig. 1) between the conducting bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts (abbreviated as ET) which can be achieved by pressure[6–8] or by changing the insulating block layers stacked along the $b$ axis.[6]

According to Ref. 6, the Rb-based $\theta$-type organic compounds have values of $U/t$ and $V/t$ that lies between the strong insulator $\theta$-(BEDT-TTF)$_2$TlCo(SCN)$_4$ with $T_c$=250 K and the nearly metallic $\theta$-(BEDT-TTF)$_2$Cs$M$(SCN)$_4$ ($M$=Zn,Co). This proximity to the metal-insulator transition can be confirmed as $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ ($\theta$-RbZn) and $\theta$-(BEDT-TTF)$_2$RbCo(SCN)$_4$ ($\theta$-RbCo) undergoes a first-order phase transition at $T_c$=195 K toward a highly insulating state. The origin of the insulating state below 195 K is found to be related to an ordering of the charges with a wave vector $q_2=(0,0,1/2)$ arising from the off-site Coulomb repulsion $V$ and commonly known as charge ordering (CO).[10] Although the origin of the insulating state below 195 K is well understood, the high-temperature state above 195 K remains a mystery. NMR,[11] x-ray diffraction,[9,10] and infrared, Raman spectroscopy[8] do detect some sort of charge disproportionation above $T_c$ from the presence of broad peaks which are sometimes interpreted as short-range CO. The wave vector of the short-range CO is, however, unrelated to the one below $T_c$. The x-ray diffraction[9,10] data is particularly difficult to understand as it reveals a diffuse spot characterized by the wave vector $q_1'=(1/3,k,1/4)$ which is unrelated to $q_2$. The diffuse spot at $q_1'$ has so far been interpreted in terms of charge fluctuations.

In order to gain more insight of this anomalous high-temperature state in $\theta$-RbZn and $\theta$-RbCo, we have measured the resistivity, $\rho$, and the thermopower, $S_b$, and extended the measurements to temperature as low as 50 K by quenching the materials. We show that the state above 195 K can be modeled as a combination of both localized and free carriers.

## EXPERIMENTAL METHOD

Single crystals were grown by electrochemical oxidation method described in details in Ref. 6. Samples were mounted in a four-wire configuration consisting of two gold wires current contacts attached at the extremes of the samples and two chromel-constantan thermocouples attached thermally and electrically at two points along the sample.[12] The two constantan wires were also used to measure the voltage drop along the sample and care was taken to subtract the thermopower contribution of the constantan to the voltage signal when temperature gradients were applied. $S_b$ and $\rho$ were measured alternatively every minute on the same sample. $S_b$ was measured using a steady-state technique and the value

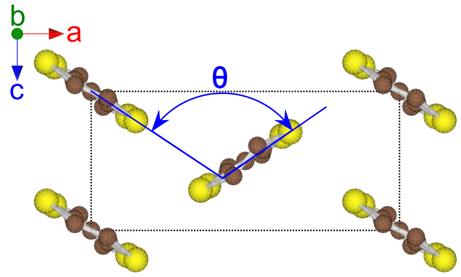

FIG. 1. (Color online) Arrangement of the ET molecules along the $b$ axis. The dotted rectangle represents one unit cell of the I222 crystal structure (Ref. 9).

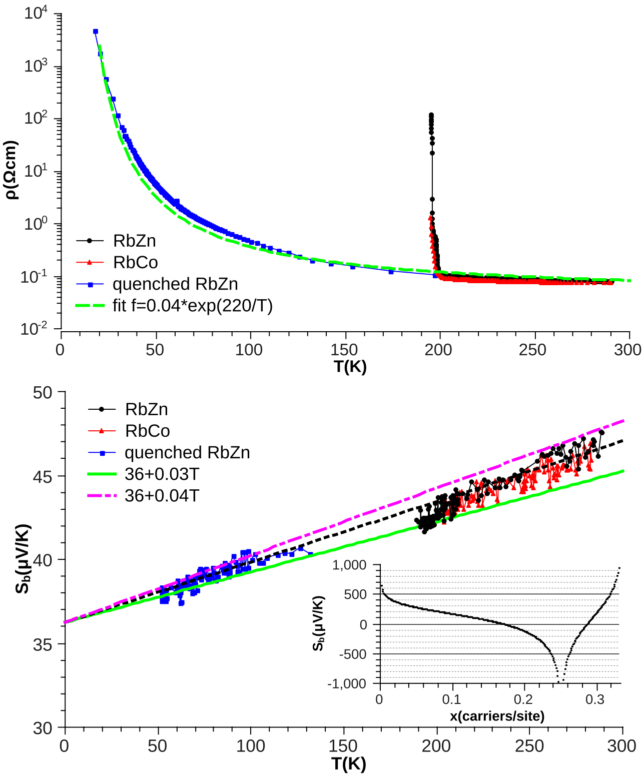

FIG. 2. (Color online) (Top) Temperature dependence of the $c$ axis resistivity, $\rho$ of $\theta$-RbZn and $\theta$-RbCo. When slowly cooled, both organic compounds go through a first-order phase transition at $T_c \approx 195$ K, where $\rho$ increases abruptly. (Bottom) The temperature dependence of the $c$ axis thermopower $S_b$ of $\theta$-RbZn and $\theta$-RbCo. The values of $\rho$ and $S_b$ below 195 K are related to the quenched high-temperature state of $\theta$-RbZn. The sample was measured between 130 and 50 K in both cooling and warming stage. The quenching temperature is from 210 to 130 K where the metastable state is considered stable during several hours (see Fig. 3). Dotted line is the linear fit of the thermopower data. The green (solid) and magenta (dash-dotted) lines are theoretical fittings (see text). (Bottom inset) Doping dependence of Eq. (5).

was determined by the slope of the linear least-square fit of five different temperature gradients less than 0.5 K. Samples were cooled within a liquid $^4$He cryostat. Quenching was performed from 210 K to around 120 K where the full transformation from the metastable state to the equilibrium state would take months to complete. To achieve high-cooling rates, the probe head was quickly lowered directly into the liquid $^4$He to achieve a cooling rate of at least 20 K/min through the 195 K first-order phase transition and resistivity measurements with high refresh rates were made to monitor any jumps due to cracks or significant nucleation of the $q_2$ phase.

## RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of $\rho$ and $S_b$ for both $\theta$-RbZn and $\theta$-RbCo samples. Ironically our data further confirms the deduced phase diagram of the $\theta$-based organic salts in Mori *et al.*[6] as both materials exhibit identical electronic properties while the thermopower data of $\theta$-RbCo in the same reference, Mori *et al.*,[6] is presented as different and lower than the $\theta$-RbZn data which is identical to our data. Difference in the thermopower but not in the resistivity in the same reference, Mori *et al.*,[6] between Cs compounds further highlight that the thermopower measurements in that reference are not consistent with other probes results. At 195 K a first-order phase transition occurs in both compounds which results in an abrupt increase in resistivity [Fig. 2 (top)]. The temperature dependence of the electronic state above 195 K can be best described through resistivity data as an activation-type transport with an energy gap $\delta \approx 220$ K which is very close to the reported value of $\delta \approx 200$ K from the same compound and state in Ref. 13. However, the temperature dependence of $S_b$ is very anomalous as it follows a $T$-linear temperature dependence usually related to the thermopower of metals[14] but which does not extrapolate as it should toward 0 $\mu$V/K. The intercept at $T=0$ K reaches approximately 36 $\mu$V/K, which is quite substantial. We can confirm these trends by quenching the material so as to freeze the high-temperature phase and extend $\rho$ and $S_b$ to temperatures as low as 50 K. Note that $S_b$ was unable to be measured accurately from 130 to 190 K as the rapidly cooled state decomposes too quickly to the equilibrium phase. The anomalous nature of the temperature dependence of $S_b$ is similar to the case of the normal-state thermopower of the high-$T_c$ copper oxides[15,16] and to the thermopower of the misfit cobalt oxides.[17] However a few very important differences between these systems exist. For instance, both the slope of the $T$-linear contribution to $S_b$ and the sign of the shift in $\theta$-RbZn and $\theta$-RbCo indicate a hole charge carrier while in the case of the high-$T_c$, the slope of the $T$-linear contribution and the shift indicate a hole and an electron contribution. In the case of the misfit cobalt oxide, both the slope and the shift indicate a hole contribution like in our data. However unlike our data, the thermopower $T$-linear slope of the misfit cobalt oxides[17] is very large which would indicate a very large effective mass of the carriers while the shallow $T$-linear slope of our data would indicate carriers with an effective mass close to the bare electron mass.

To emphasize how strange the temperature dependence of $S_b$ is, the total $S_b$ of a system with different group of carriers, $i$, is written as

$$S_{b\ total} = \frac{\Sigma \sigma_i S_{b,i}}{\Sigma \sigma_i}, \tag{1}$$

where $\sigma$ is the conductivity. Equation (1) highlights that it is extremely unlikely that $S_b$ can exhibit both a $T$ linear and a $T$-independent contribution from two different groups of carriers as both group should have a very different temperature dependence of the conductivity. A system with a phase separation would require the additional complication of the thermal conductivity difference between the phases to be included into the equation as in the case of the manganite $La_{2/3}Ca_{1/3}MnO_3$.[18] Thus it is even less likely that a phase separation could explain the temperature dependence of $S_b$ in $\theta$-Rb$M$ ($M$=Zn, Co). Furthermore, the absences of magnetic order at those temperatures[6,11] excludes any significant changes from the spin channel entropy contribution of ln 2. Nevertheless $\theta$-Rb$M$ ($M$=Zn,Co) does exhibit both metallic and insulating behaviors that can be clearly seen through ac resistivity measurements[13,19] where the dielectric constant is found to be positive and large with a relaxation-type frequency dependence. As such the only way to reconcile this dual nature and the temperature dependence of $S_b$ with Eq. (1) is to have only one group of carriers which exhibit both metallic and insulating character. This state is, however, highly anomalous and can only arise from an exotic state like a "pinball-liquid" state[20,21] where both itinerant and localized charges coexist.

To justify our interpretation that the anomalous temperature dependence of $S_b$ is the result of the same charges being both localized and itinerant, we will quantitatively evaluate $S_b$ using a zeroth-order approximation. To this end we first introduce for notation purpose the Hamiltonian of a spinless fermion system within a $t$-$V$ model (an extended Hubbard model) as

$$H = -\sum_{\langle ij\rangle} t_{ij}(c_i^\dagger c_j + \text{H.c.}) + \sum_{\langle ij\rangle} V_{ij} n_i n_j, \qquad (2)$$

where $c_i^\dagger(c_i)$ is the creation(annihilation) operator of fermions at site $i$ and $n_i$ $(=c_i^\dagger c_i)$ is the number operator. The index $\langle ij\rangle$ are the nearest-neighbor pair sites. $U$ $(=V_{ii})$ and $V$ $(i\neq j)$ are, respectively, the on-site and intersite Coulomb interactions. We have assumed a spinless state because $U$ is large enough to prohibit the double occupancy on the same site. We have previously stated that $\theta$-Rb$M$ ($M$=Zn,Co) has a first-order phase transition to a long-range CO at 195 K. This CO can be understood in this system if we assume that $t < V < U$. Therefore we are not dealing with a quarter filled system of holes but a half-filled system of spinless fermions $(x=1/2)$.

We begin our quantitative estimate of $S_b$ by interpreting the intercept of 36 $\mu$V/K as a temperature-independent contribution. Heikes formula expresses such a temperature dependence of $S_b$ in a narrow band (NB) system with $t \ll k_B T$. The well-known form of the Heikes formula refers to the temperature-independent thermopower value at the high-temperature limit of noninteracting spinless Fermions and is expressed as

$$S(T\to\infty) = \frac{-k_B}{e}\ln\frac{1-x}{x}, \qquad (3)$$

where $x$ is the ratio of charge carriers $N$ to sites $N_A$ $(x=N/N_A)$ and $e$ is the absolute value of the electron charge. Carriers with spin and interactions such as $U$ and $V$ can be included to derive Heikes formula[22] for systems with localized interacting particles at temperatures much greater than $t$. However to derive these generalized Heikes formula, the degeneracy of the system which depends on the dimensionality, the spin state, $U$, $V$, and $\rho$ must be known.

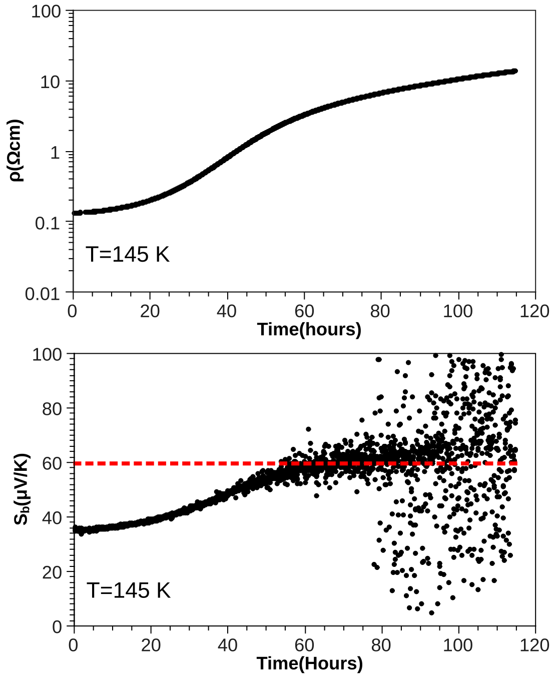

FIG. 3. (Color online) Time dependence of the $c$ axis resistivity (top) and $S_b$ (bottom) of $\theta$-RbZn at 145 K during the spinodal decomposition from the $q_1'$ state to the $q_2$ state. The 60 $\mu$V/K dashed red line is the value of the Heikes formula for localized charges carriers with full spin degeneracy.

We have already stated that we have no magnetic order and as such we would expect a minimum contribution of $k_B/e\times\ln(2)\approx 60$ $\mu$V/K if the charge carriers were localized in a fix pattern. To test this assumption in $\theta$-RbZn and $\theta$-RbCo, we have tried to estimate the thermopower of the long-range $q_2$-type CO state where all the charge carriers are localized in a fixed pattern. However direct measurement of the thermopower of the $q_2$-type CO state is impossible as the very large values of the resistivity induce Johnson-noise voltage level too high to accurately estimate the thermopower value. As such we have measured, at various temperatures, the resistivity and the thermopower of the rapidly cooled state decomposition to the $q_2$-type CO equilibrium phases (i.e., a spinodal decomposition) so as to extrapolate an estimate of the thermopower of the $q_2$-type CO state. Figure 3 shows the typical evolution of $\rho$ and $S_b$ during the spinodal decomposition at 145 K of $\theta$-RbZn. $S_b$ is found to increase from the values shown below 195 K in Fig. 2 as the volume fraction of the $q_2$ CO state progressively replaces the $q_1'$ state and saturates close to the predicted 60 $\mu$V/K value. Reproducibility of this trend at different isothermal temperatures above 130 K reveals that $S_b$ always saturates close to the 60 $\mu$V/K value. Furthermore, a systematic study of the spinodal decomposition with x-ray[23] data and resistivity measurements has revealed that the decomposition follows a classic Kolmogorov-Johnson-Mehl-Avrami equation[24] with an activation energy of approximatively 0.45 eV. Although the resistivity value in Fig. 3 after 120 h is still not close to the equilibrium-state value, in term of volume fraction the $q_2$ state occupies already more than 90% of the total volume after 45 h at this temperature. These results confirms that charge carriers localized in a fixed pattern and with no magnetic order should yield a thermopower value of 60 $\mu$V/K in these compounds. As we have no magnetic ordering in both phases at temperature above 30 K, the NB charges of the high-temperature state must have some degree of degen-

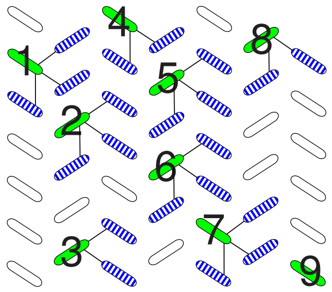

FIG. 4. (Color online) Example of a filling pattern of NB charges. The number represents the order we randomly put the NB charges (full green sites) starting from the top-left corner and going down each vertical line from left to right. The striped blue sites are forbidden sites for NB charges due to nearest-neighbor Coulomb repulsion and the filling pattern.

eracy related to their location so as to obtain a value of the thermopower less than 60 $\mu$V/K. This point is essential and highlight a huge difference with the case of the misfit cobalt oxides[17] where the thermopower shift of the $T$-linear thermopower is attributed to a spin-charge separation where charges are delocalized and the spins are localized and contribute a constant 60 $\mu$V/K.

If we assume that $t, V \ll k_BT \ll U$ then by using Heikes formula,[22] we would need an unrealistic $x \approx 0.57$ holes per ET sites to achieve $S_b \approx 36$ $\mu$V/K. Therefore we must assume that the nearest-neighbor Coulomb repulsion, $V$ is such that $t \ll k_BT \ll U, V$. To model the spatial degeneracy of the NB charges, we use the same calculation principle defined in Ref. 22 but in a two-dimensional triangular lattice. The degeneracy is calculated for a system with $N_A$ sites arranged, for example, like in Fig. 4. We put $N$ charge carriers randomly along the vertical axis (i.e., $c$ axis) starting from the top-left corner and going down each vertical axis. After finishing one vertical axis we continue to randomly put the charge carriers to the next vertical axis on the right starting from the top and go on until we use $N$ sites. To ensure that the nearest-neighbor sites are empty with this filling pattern, we mark three sites on the bottom and right of the NB charge as forbidden sites to put the next NB charge (blue hatched sites in Fig. 4). Thus within a very large network of $N_A$, ET sites and $N$ NB charges, we have $4N$ sites that are taken. Therefore the number of possible sites to place our NB charges is at least reduced to $N_A - 3N$. The spacial degeneracy of such a system is

$$g = {}_{(N_A-3N)}C_N = \frac{(N_A-3N)!}{N!\,(N_A-4N)!}. \qquad (4)$$

Using the Stirling approximation and differentiating with respect to $N$, $S_{b,NB\ charge}$ is written as

$$S_{b,NB\ charge} = \frac{k_B}{e}\ln\left(\frac{2(1-4x)^4}{x(1-3x)^3}\right), \qquad (5)$$

where we have added a ln(2) factor for the spin degree of freedom. Equation (5) is plotted in Fig. 2 (bottom inset) and yields a doping dependence which diverges at $x=0$, 1/4, and 1/3. The divergence at 0 and 1/3 is related to the under and over-filled states, respectively, while the 1/4 divergence is related to the special case of CO of the NB charge every two sites along the $c$ axis like the $2 \times 2$ CO pattern in Ref. 25. Finally using Eq. (5) we can deduce that the average hole concentration per ET site to get 36 $\mu$V/K is $x \approx 0.29$ or 0.16. As noted in Ref. 22, we have excluded some states by the way we have counted. However like in Ref. 22, the additional degeneracy should not change Eq. (5).

The $\theta$-type organic compounds are two-dimensional systems[8] with the conducting planes set perpendicular to the $b$ axis. Thereby, in the lowest-order approximation, the diffusion part of $S_b$ for a two-dimensional metal is expressed as

$$S_b = -\frac{\pi^2}{3}\frac{k_B}{e}\frac{k_BT}{E_F}, \qquad (6)$$

where $E_F$ is the Fermi energy. If we assume a free-electron approximation, then $E_F$ in a two-dimensional spinless system can be expressed as

$$E_F = \frac{\hbar^2}{2m^*}(2\pi n), \qquad (7)$$

where $n$ is the hole concentration. As $x_{total}=0.5$ and $x_{NB\ charge} \approx 0.29$ or 0.16 NB charge per ET molecule, the concentration of fermionic (F) charges is $x_{Fcharge} \approx 0.21$ or 0.34 per ET sites. However this is not correct as only the F charges can occupy the sites the NB charge have not taken yet. Thus the effective F charge concentration is $x_{Fcharge}^{eff} = x_{Fcharge}/(1-x_{NB\ charge}) \approx 0.29$ or 0.4 which using Eqs. (6) and (7) give us a slope of $\approx 0.04$ or $\approx 0.03$ $\mu$V K$^{-2}$, respectively, for a bare electron mass. Figure 2 shows that we get a reasonable fit with the data for both doping levels of the NB charge. We should highlight that these proportions of NB and F charges represent an average of such states, we expect charges to fluctuate between NB and F states like in the "pinball-liquid" model.[20,21]

## CONCLUSION

In conclusion, we have shown that the anomalous temperature dependence of $S_b$ in $\theta$-Rb$M$ ($M$=Zn,Co) can be understood as an exotic state where the same charges exhibit both itinerancy and localized characters. Furthermore the $S_b$ data highlights that the localized contribution to $S_b$ cannot come form a perfect pattern of charge carriers. Further theoretical study will be required to fully understand the nature of anomalous temperature dependence of $S_b$ in $\theta$-Rb$M$ ($M$=Zn,Co).

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