Possible origin of nonlinear conductivity and large dielectric constant in the commensurate charge-density-wave phase of $1T$-TaS_2

Yongchang Ma,[1,2,3,*] Yanhui Hou,[1] Cuimin Lu,[1,4] Lijun Li,[2,†] and Cedomir Petrovic[2]
[1] *School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China*
[2] *Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA*
[3] *Key Laboratory of Display Materials and Photoelectric Devices (Tianjin University of Technology), Ministry of Education, Tianjin 300384, China*
[4] *Tianjin Key Lab for Photoelectric Materials and Devices, Tianjin 300384, China*

(Received 27 June 2017; revised manuscript received 18 April 2018; published 10 May 2018)

The electric field dependence of the dielectric properties and the nonlinear conductance of $1T$-TaS_2 below 50 K has been investigated. A large dielectric constant of about 10^4 is obtained up to 10^7 Hz, which cannot be attributed to hopping of the localized carriers alone, the collective excitations of the commensurate charge-density-wave must be another contributor. The dielectric spectra disperse slightly in our measured temperature and frequency range. At a moderate dc bias field, the real part of the dielectric constant $\epsilon_1(\omega)$ decreases. We propose that the separation of bound soliton-antisoliton pairs may be a contributor to the reduction of $\epsilon_1(\omega)$ and the accompanying nonlinear conductivity with increasing dc bias.

DOI: 10.1103/PhysRevB.97.195117

I. INTRODUCTION

Nonlinear conductivity and large polarization effects are the well-known phenomena in charge-density-wave (CDW) systems [1–3]. Though researchers have made considerable progress in understanding the associated transport properties in quasi-one-dimensional CDW compounds [4–12], less discussions for two-dimensional (2D) CDW crystals have been carried out, especially the polarization properties [13–17]. In recent years, the investigation of 2D CDW compounds has been revitalized, because they would be helpful in understanding the mechanisms of the high-T_c superconductors [18–20] and the origin of ultrafast switching to a stable hidden quantum state [21,22]. Hence, it is of interest to investigate the charge transport behavior in 2D CDW systems.

A 2D CDW often reveals itself in layered transition-metal dichalcogenides and rare-earth tritellurides [13,14,23–26]. Researchers began to study the charge transport properties of 2D CDW systems ($1T$-TaS_2) about 40 years ago. References [14,27,28] suggested that the carriers localization induced by disorder may be responsible for the unique low-temperature transport properties, whereas Uchida *et al.* [16] proposed that the nonlinear conduction in the presence of a moderate electric field at low temperatures might be explained by the collective excitations in pinned CDWs—the creation of a soliton in a pair with an antisoliton. In the subsequent experiments, though the electronic nature was probed by various powerful spectroscopies [29–33], until recent years the mechanisms for the charge dynamics of the commensurate CDW (CCDW) phase in $1T$-TaS_2 had not been disclosed yet. The discrepancy in understanding the transport properties at low temperatures has prompted us to study the fundamental question of whether the collective excitations of CCDW exist in $1T$-TaS_2. As proposed by Rajaraman [34], for a system described by the equation of motion with soliton solutions, the soliton-antisoliton "doublet" also exists, in which the equally but oppositely charged solitons are in confinement and lead to a large static dielectric constant [35]. Since localized electrons have a distinct role in the dispersion of the dielectric spectrum, $\epsilon_{r1}(\omega) \propto \omega^s$ (s < 0) [36,37], investigations of the dielectric properties of $1T$-TaS_2 would be helpful to demonstrate whether the doublets have an essential contribution. On the other hand, by applying a dc electric field, the bound charges in the soliton-antisoliton doublets may obtain a larger probability to decouple into carriers with long mean-free-paths and accordingly drive a nonlinear conductivity superposing on the Ohmic behavior.

A temperature- and field-dependent complex dielectric or conductivity spectrum is a powerful probe for investigating the charge transport and polarization behavior of various systems [9,10,38–41]. At a fixed temperature T_0, the complex dielectric or conductivity spectrum is ultimately defined by the polarization or conductance of the total contributing charged microscopic particles. In quasi-1D CDW systems, exceptionally large dielectric constants with strong dispersion and novel conducting behavior in radio and audio frequencies were observed [1,10,42]. Further, the dc-biased charge dynamics would be of great interest, since nonclassical characteristics often reveal, e.g., the well-known current oscillations and mode-locking [1]. Clearly, these novel properties should not be attributed to normal carriers but to the newborn current-carrying mechanisms associated with CDWs by applying an electric field. For $1T$-TaS_2, the non-ohmic behavior manifests in a current-voltage characteristic (CVC), naturally it is expected to be relevant to individual particles or collective

*ycma@tjut.edu.cn
†Permanent address: Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China.

 ©2018 American Physical Society

excitations of CDW condensates [16,17]. To the best of our knowledge, the discussions on dielectric or ac conductance behavior in 2D CDW systems are limited, possibly due to strong screening effects from normal carriers thermally excited over the nonuniform CDW gap opening at the Fermi level [29,31]. Usually, normal carriers respond extremely fast ($< 10^{-12}$ s), and if their density is large enough, the features of the conductivity in radio and audio frequencies relevant to the excitations of CDW condensates will become too weak to be identified well. However, below $T = 50$ K, the number of normal electrons excited by thermal energy remarkably decreases [14,21], providing good opportunities to clarify the mechanisms of carriers' motion in the CCDW phase of $1T$-TaS_2.

In this article we systematically study the polarization properties of $1T$-TaS_2 flakes below 50 K. To clarify the origin of the nonlinear conductance in a CVC, the dielectric properties under various dc biases, E_B, are also probed. The Joule-heating effects on ac conductivity under a constant bias field of $E_B \leqslant 20.0$ V/cm are analyzed by comparing them with the pulsed approach. We propose that the large relative dielectric constant ($\epsilon_r \sim 10^4$) up to frequency 10^7 Hz cannot originate mainly from the hopping process of the localized states, but is possibly driven by the existence of bound soliton-antisoliton pairs (BSPs). Besides the hopping of localized carriers, the separation of BSPs may also be the driving force for the reduction of $\epsilon_1(\omega)$ and the nonlinear conductivity with increasing of dc bias.

II. EXPERIMENT

The $1T$-TaS_2 single crystals were successfully grown by the conventional chemical vapor transport method in a gradient furnace. The stoichiometric tantalum and sulfur pieces were put into an alumina crucible before being sealed in a quartz tube and prereacted at 900 °C for 50 h and then cooled to 760 °C within 12 h followed by natural cooling. For single crystals' growth, the temperature of the hot (cold) end was 900 °C (800 °C). After 1 week of growth time, the quartz tube was quickly pulled out and then quenched into cold water. Consistent with the earlier reports [24], the as-grown single crystals show thin flakelike shapes and gold-shining color, with typical sizes in the range $(3 \sim 10) \times (2 \sim 3) \times (0.02 \sim 0.08)$ mm^3. Reference [28] shows $\rho_\perp/\rho_\parallel \sim 500$ over the range $1.3 < T < 240$ K, where $\rho_\parallel$ and $\rho_\perp$ are the resistivity perpendicular and parallel to the layers of the $1T$-TaS_2 crystal, respectively, indicating an essential 2D system. In the experiments, we focused on the in-plane polarization and transport properties of the sample with a surface area of 3.0×0.4 mm^2 and a thickness (along the c axis) of about 25 μm, and the distance between two potential contacts was about 1.0 mm.

Temperature-dependent resistivity was measured with the current $I = 10$ μA before probing the dielectric spectra. The CVCs showed linear behavior in a weak electric field, confirming good ohmic contacts by silver paste. We also compared the contact resistance of the four-contact and two-contact probes and found the difference was negligible compared to the sample resistance from 300 to 12 K. The Hall coefficients were probed under a magnetic field $H = 10.0$ kG parallel to the c axis of the sample. In addition, we confirmed that the impedance spectra were unaffected by the difference between substrates by comparing data obtained with sapphire and the ultrathin mica sheets. The complex impedance properties under various dc biases up to 40 V/cm $\hat{z}(\omega) = |\hat{z}(\omega)|\cos\theta(\omega) + i|\hat{z}(\omega)|\sin\theta(\omega)$ were probed on an Agilent 4294A precision impedance analyzer through four-coaxial cables in two pairs (corresponding to two electrodes on the sample), where $\theta(\omega)$ was the phase difference between the ac driving potential and the response current at frequency ω. The sample was mounted on a cryostat of a closed-cycle refrigerator (JANIS) with the experimental temperature range from 12 to 300 K monitored by a Cryo·con 32 temperature controller. All the impedance spectra were measured with a driving voltage of 30 mV (rms), where the nonlinear conductance does not appear in I-V measurements. In analysis, the sample was seen as a leakage capacitor, both the dielectric constant $\hat{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and the complex conductivity spectrum $\hat{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ could be deduced from the raw data $\hat{z}(\omega)$ based on the universal relations $\hat{\epsilon}(\omega) = \frac{\hat{\sigma}(\omega)-\sigma_{dc}}{i\omega}$ and $\hat{\sigma}(\omega) = 1/\hat{z}(\omega)$; thus $\epsilon_1(\omega) = \frac{-\sin\theta(\omega)}{\omega|\hat{z}(\omega)|}\frac{d}{S}$, where $\epsilon_i(\omega) = \epsilon_0\epsilon_{ri}(\omega)$ ($i = 1$ and 2), and d and S are the length and the cross-sectional area of the sample, respectively.

III. RESULTS AND DISCUSSION

The temperature-dependent resistivity $\rho_{dc}(T)$, the CCDW transition temperature $T_{\text{CCDW}} = 180$ K, and the hysteresis feature upon warming are all consistent with previous reports [17,21,23], indicating good quality of the $1T$-TaS_2 single-crystal samples. The existence of nonlinear conductivity in the CCDW phase was confirmed, as shown in Fig. 1. In our experiments, the electric field is limited within a moderate range, no more than 20 V/cm. The previous data have already shown that the carriers in the CCDW phase of $1T$-TaS_2 are positively charged and the density is larger than 10^{19}/cm^3; hence the interface or the contact effects induced by the Schottky barrier can be neglected. In the following, the experimental data were obtained upon decreasing temperature in the CCDW phase. We

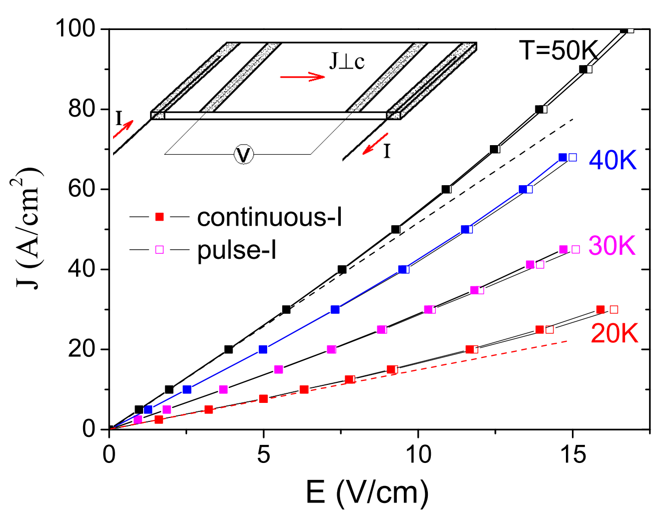

FIG. 1. The current voltage characteristics of the $1T$-TaS_2 crystal at various temperatures below 50 K. The inset is a drawing of the experimental measurement geometry.

focus on the polarization behavior of $1T$-TaS_2 in the presence of the nonlinear conductance below $T = 50$ K.

To obtain the intrinsic CVCs, a narrow-width pulsed-current method is often required [4,16,17]. However, to investigate the polarization properties of the $1T$-TaS_2 single crystals in the presence of the nonlinear conductivity, a continuous dc bias would inevitably heat the sample (the Joule-heating effects). The only question is how much does it change the temperature of the sample. Considering that the nonlinear conductance was present in a moderate field, we compared the difference between the pulsed approach with a pulse duration of 0.1 ms and the continous method below $T = 50$ K (see Fig. 1). At different temperatures, the data are similar except the initial slopes of the CVCs. Below $E = 5.0$ V/cm at a fixed temperature, the CVCs differ only slightly, indicating a trivial Joule heating, whereas above $E = 8.0$ V/cm, a deviation starts to appear. Generally, it is shown that self-heating has strong effects on dc transport properties in all systems with a negative temperature coefficient of resistance [43,44].

A. The self-heating effects to conductivity spectrum under dc bias

The self-heating in an external dc field and its influence on transport properties is important. To clarify this effect, the CVC at $T = 30$ K in a wide electric field range was obtained [see Fig. 2(a)]. For the current in continuous mode, an extra conductivity is superimposed on the pulsed results, indicating the effect of local Joule heating (the self-heating effect), not the intrinsic properties of the $1T$-TaS_2 system.

For the conductivity and dielectric spectra measured at constant dc bias using small ac voltage with changing ω, at low frequency, $\sigma_1(\omega \ll 1/\tau_{SH})$ is proportional to the differential conductivity (dI/dV), where τ_{SH} is the relaxation time from self-heating, at high frequency, $\sigma_1(\omega \gg 1/\tau_{SH})$ is proportional to the chordal conductivity (I/V). τ_{SH} is related to the specific heat by the expression $[\tau_{SH} = \frac{N_M c}{\kappa}\frac{d}{S}]$, where N_M is the number of moles of material with specific heat c and thermal conductance κ [45]. In our experiments, $N_M \simeq 2.8 \times 10^{-7}$ mol, $c = 5.0$ J/mol K at 30 K [46], and τ_{SH} is estimated to be approximately milliseconds for heat flow parallel to the ab plane, larger than the perpendicular direction [47–49].

Nevertheless, above 10 kHz the thermal relaxation effect under E_B nearly disappears [Fig. 2(b)], being consistent with the measurement in the pulsed approach with a duration of 0.1 ms. However, an increase of frequency does not remove the local Joule heating. Specifically, the total conductivity $\sigma_T = \sigma_{NM} + \sigma_{NL} + \sigma_{SH}$, where the subscripts NM, NL, and SH represent the contribution of normal carriers, the nonlinear conductance, and the self-heating effect. These three components behave differently with increases in frequency. σ_{NM} should reveal the well-known Drude free-electron properties and has no dispersion below GHz. σ_{NL} remains unresolved at present, whereas for σ_{SH}, because the averaged temperature of the sample elevates under dc bias, thus an increase of the frequency-independent conductivity is expected, since $1T$-TaS_2 is a system with a negative temperature coefficient of resistance.

In order to study the charged dynamics in the presence of the nonlinear conductance in $1T$-TaS_2, the evaluation of the

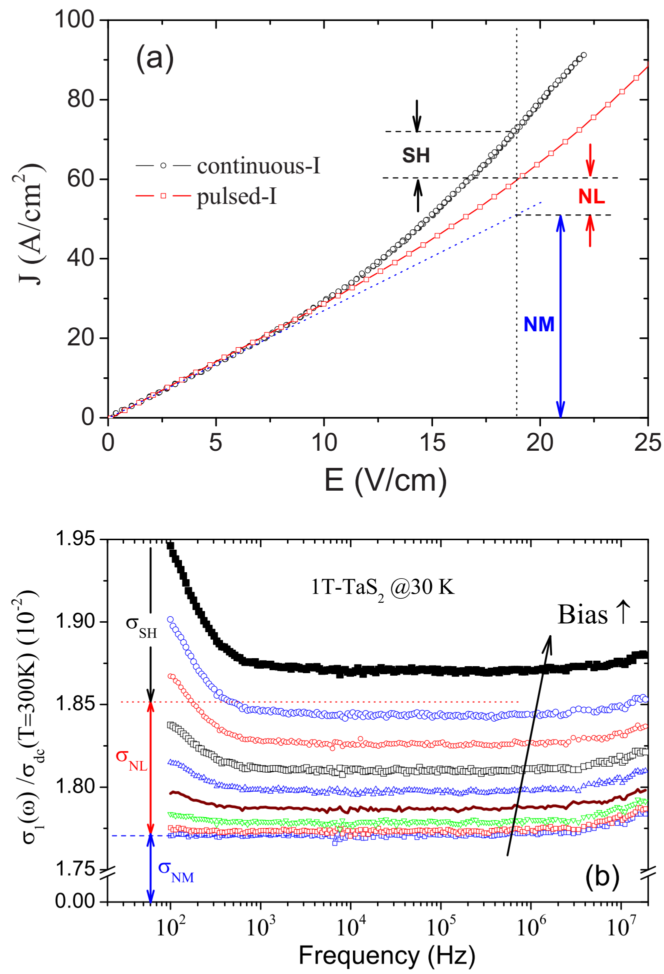

FIG. 2. (a) The current-voltage characteristics up to 25 V/cm of the $1T$-TaS_2 crystal at 30 K. (b) The conductivity spectra of the $1T$-TaS_2 crystal at 30 K normalized to the dc conductivity at 300 K under various dc biases (from bottom to top, 0, 1, 2, 3, 4, 5, 6, 8, and 10 V/cm). The notations SH, NL, and NM are the conductivity from self-heating, nonlinear conductance, and normal carriers, respectively. The dotted-line in panel (b) presents σ_{NL}, which is obtained from the CVC results where the self-heating effect could be neglected in the pulsed approach with a duration of 0.1 ms and a magnitude of 10 V/cm (solid square).

temperature elevation under dc bias is necessary. We compare $\sigma_1(\omega)$ in Fig. 2(b) at 10 kHz with the CVC results measured in the pulsed approach and find that the enhancement of the averaged temperature at bias 10 V/cm is no more than 0.5 K in our experimental configuration. Above several MHz, $\sigma_1(\omega, E_B = 0)$ increases with increasing frequency. Clearly, this behavior should not originate from normal carriers or a thermal effect, but rather should be associated with a large dielectric constant.

B. The large dielectric constant in the MHz region

In 1D CDW systems, the exceptionally large dielectric constants and strong dispersion in the audio frequency range have been extensively investigated [9,10,42,50]. However, the investigations of dielectric behavior are rarely reported for

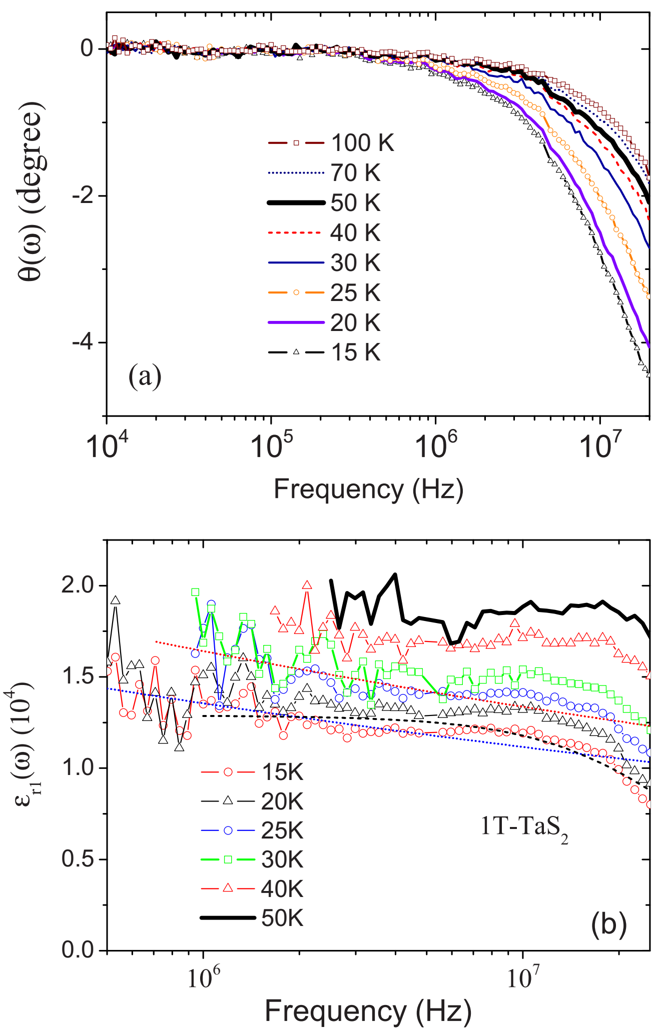

FIG. 3. (a) The spectra $\theta(\omega)$ of $1T$-TaS_2 in the CCDW phase at various temperatures below 100 K. (b) The temperature-dependent dielectric constant of $1T$-TaS_2 in the MHz region below 50 K. Note that the dotted lines using the hopping model alone cannot fit the data well at $T = 15$ and 25 K, while the dashed lines (hopping + Debye) provide good-fitting results.

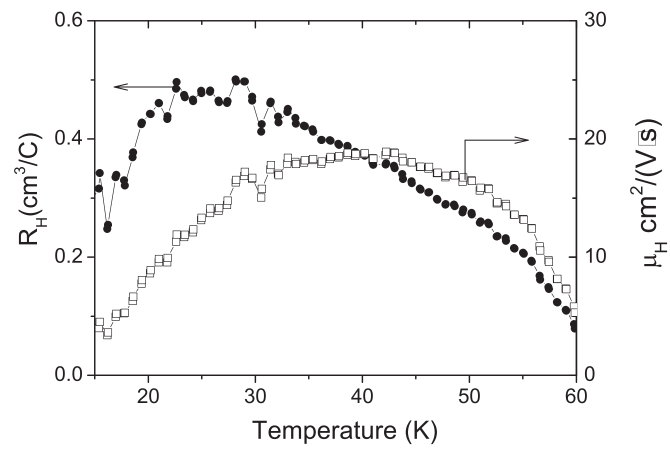

FIG. 4. The temperature-dependent Hall coefficient and the carriers' mobility of the $1T$-TaS_2 crystal below 60 K.

2D CDW compounds, possibly due to the large screening effects from the normal carriers excited over the nonuniform CDW gap opening at the Fermi surface. Nevertheless, for the polarization properties of the 2D CDW system $1T$-TaS_2, a large static dielectric constant is expected for its highly polarizable structure, as suggested by Vaskivskyi *et al.* [17]. In our experiments, relatively small minus $\theta(\omega)$ could be identified below $T = 100$ K, revealing capacitive responses, as shown in Fig. 3(a). For dielectric spectra $\epsilon_{r1}(\omega)$, there is much noise below 2.0 MHz, whereas a distinct decrease could be identified above 10^7 Hz [see Fig. 3(b)]. At present, we cannot obtain complete relaxation behavior of the corresponding polarization process for the limited measuring frequency range. With decreasing temperature below 50 K, the dielectric spectra are suppressed, whereas the line shapes remain unchanged.

The large dielectric constant ϵ_{r1} of the order of 10^4 in the MHz region is of interest. In the incommensurate CDW system, extremely large polarization effects are expected due to weak pinning from impurities or defects [51]. For the CCDW state in $1T$-TaS_2, unlike the incommensurate 2D system $TbTe_3$ where Sinchenko *et al.* observed CDW sliding [25], it would be difficult to slide in a moderate electric field due to the strong pinning by the underlying lattice and hence the contribution to the static dielectric constant would be much smaller [51]. Here one may argue that the mechanism in establishing the colossal dielectric constant in $(NbSe_4)_3I$ (due to the slight shift of the single chains against each other) can be a potential substitute for $1T$-TaS_2; however, such similar features of the lattice structure have not been identified yet [10].

As discussed by Lunkenheimer *et al.* [36], the hopping process of localized states can also give rise to large values of the dielectric constant. In Ref. [28] Hambourger and Di Salvo suggested that the disorder-induced localization may explain the transport properties in the $1T$-$TaS_{2-x}Se_x$ system, as supported by Dardel *et al.* [29] and Kim *et al.* [30]. Indeed, our data of the temperature-dependent Hall coefficient (Fig. 4) is consistent with Ref. [28], indicating the occurrence of carriers' localization in the single-band approximation. However, we note that the dielectric spectrum cannot be fitted well by the hopping process alone [36,37,52]: $\epsilon_{r1}(\omega) \propto \omega^s$ $(s < 0)$. In Fig. 3(b), the dotted-curve fittings with $s = -0.08$ show a slightly upward curvature, which is inconsistent with the experimental data exhibiting a downward curvature above 10 MHz. Clearly, the cases at other temperatures behave similarly. Hence it seems that a relaxation process must exist besides the hopping of localized electrons based on the dielectric properties. On the other hand, the interfacial effects, such as a grain boundary or a surface depletion layer, also contribute to colossal dielectric constants. However, the positively charged carriers with density larger than $10^{19}/cm^3$ in the CCDW phase exclude the Schottky-barrier effects. As for the polaron contribution to the dielectric constant, we note that in the infrared conductivity spectrum, no such characteristic could be identified without photoexcitations [53].

We propose that the polarization properties of $1T$-TaS_2 could be described by the well-known soliton model used in 1D CDWs. To the best of our knowledge, the complete theoretical model for the phase solitons in 2D CDW materials is not available at the moment. The existence of CDW phase solitons—topological phase defects—is a particular form of collective excitation in the CDW condensate and has been confirmed in quasi-1D systems [54–57]. Recently, there are suggestions that soliton contribution must be rather important for the unconventional transport properties associated with CDW systems [58–60]. Rojo-Bravo *et al.* [61] indicated that the transport mechanism of traveling soliton lattice may open new perspectives in controlling correlated charges over long distances, explaining the main features of sliding CDW systems.

In Ref. [35], Krive and Rozhavsky proposed that the phase solitons significantly contribute the dielectric susceptibility. As shown in Fig. 5(a), the localized compressions or rarefaction in the local condensed electron density (or deformations of the CDW phase φ) correspond to the soliton-antisoliton pair. A sketch of the charge density and the lattice arrangement is shown in Fig. 5(b) [36,62]. It is plausible that the central Ta atoms attract more electronic cloud which favors the commensurate CDW. In the equation of motion relevant to the CDW phase, $d^2\varphi/dt^2 - c_0^2\nabla_x^2\varphi + \omega_F^2 dV(\varphi)/d\varphi = 0$, where c_0 is a characteristic velocity of the undeformed condensate and ω_F is the pinning frequency, and the realistic pinning potential of the phase $V(\varphi)$ has a periodic form as expected [56,57]. The exact solutions of the equation should consist of several forms characteristic of solitons, including the soliton-antisoliton doublet [34], whose excitation energy is relatively lower due to the existence of coupling, compared with the case of the discreet soliton and antisoltion [see Fig. 5(c)]. Instead of separating into the discrete soliton and antisoliton which are infinitely far apart from each other in infinite time, the relative separation for the members of the doublets oscillates periodically [34]. This doublet solution is also a "breathing" one and can be thought of as a BSP.

As the equally but inversely charged phase excitations are confined in BSPs, they would contribute to the dielectric constant of the system. This can be estimated using a simple expression for the dipole oscilliator [35]: $\epsilon_\varphi \sim \epsilon_\Delta (E_s/\omega_0)\ln(E_s/\omega_0)$, where $E_s/\omega_0 = \Delta/M\omega_Q$, Δ is the energy gap in the electronic spectrum, M is the commensurability index, and ω_Q is the bare frequency of phonons with momentum $Q = 2k_F$ (Fermi wave vector). As suggested by Krive and Rozhavsky [35], $\epsilon_\varphi \ \sim 10^{1\sim 2}\epsilon_\Delta$, where ϵ_Δ is about 10^3, hence a dielectric constant of $\sim 10^4$ would be reasonable. In Ref. [16], Uchida *et al.* considered the collective excitation of a soliton in pair with an "antisoliton" under a moderate field to explain the field-independent Hall coefficient at $T = 4.2$ K. However, solitons in CDW systems are always excited in pairs; whenever a soliton (φ compression) is created, an antisoliton (φ rarefaction) appears. Though the explanation of Uchida *et al.* [16] demonstrates that mobile solitons and antisolitons are excited by applying an electric field, they can not identify whether the excitation is ground state → II or BSP → II, where II presents the state of free solitons and antisoltions [Fig. 5(c)]. Reference [16] and the associated research work [21,27,28] on the dc transport did not provide the dielectric properties of the CCDW state of $1T$-TaS_2. As bound charged microscopic states contribute to large electric polarizations, the BSPs are expected to exist.

Though the polarization properties of the BSPs are far from being understood, a Debye relaxation or Cole-Cole empirical equation may be plausible. In Fig. 3(b), good fittings to the dielectric spectra were provided by the sum of the hopping process and the Debye relaxation model: $\epsilon_0\epsilon_{r1} = \epsilon_{HF} + (\epsilon_s - \epsilon_{HF})/[1 + (i\omega\tau_0)] + A_{hp}\omega^s$, where τ_0 is a characteristic relaxation time; ϵ_s and ϵ_{HF} are the dielectric constant in static and at a higher frequency limit of the Debye relaxation model, respectively; A_{hp} is the coefficient of the hopping term; and s is assumed to be -0.2 [37,52]. The resultant parameters are shown in Table I. It is remarkable that the feature above 10 MHz is associated with the Debye relaxation, whereas the hopping

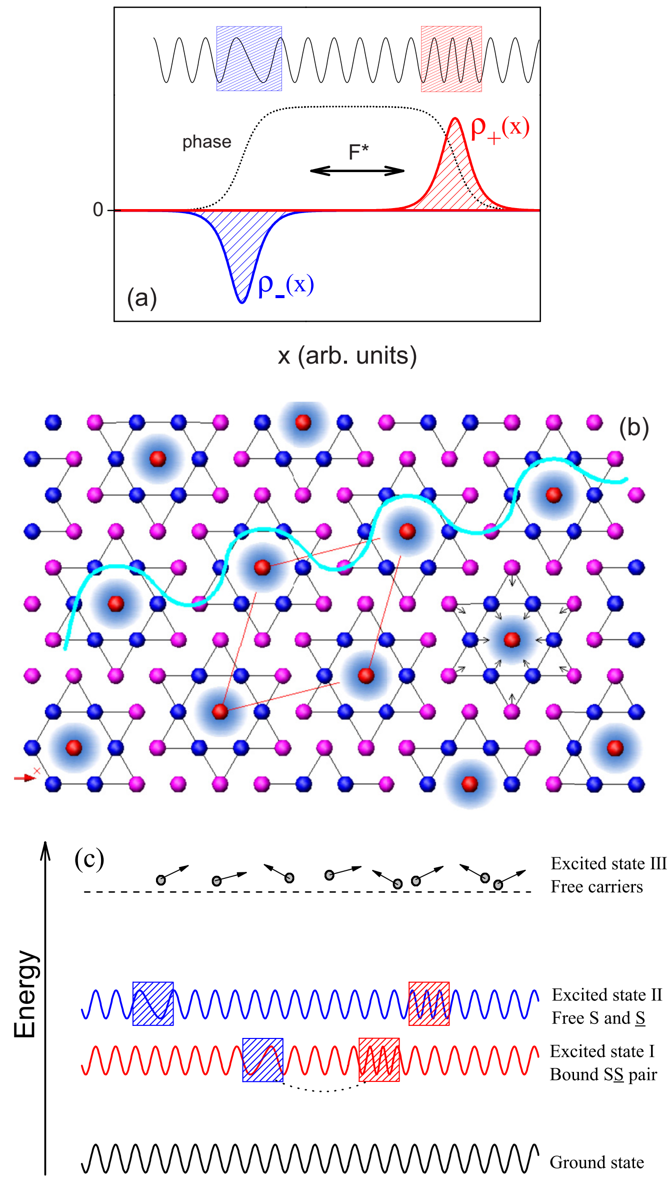

FIG. 5. (a) Real-space picture of a materialized soliton-antisoliton pair, showing the qualitatively position-dependent phase $\varphi(x,t)$ at a fixed time, excess charge density $\rho(x) \propto \partial\varphi/\partial x$ [34]. (b) The schematic pattern of the charge arrangement of $1T$-TaS_2 in real space. Note the charge ordering of the star of David cluster. The wave form stands for the commensurate charge density relative to the lattice. (c) The schematic illustration for the various excitations of the CDW condensate. Note that S represents soliton, whereas $\underline{S}$ represents antisoliton.

TABLE I. The resultant parameters for fitting the dielectric spectra of $1T$-TaS_2 at $T = 15$ K and 25 K. ϵ_{HF} is not a dominant parameter and has been determined empirically.

T(K)	ϵ_s ($10^3\epsilon_0$)	ϵ_{HF} ($10^3\epsilon_0$)	τ_0 (10^{-8} s)	A_{hp} ($10^3\epsilon_0$)
15	10.6	1.0	2.7	40
25	12.2	1.0	2.2	56

process would be responsible for the slight dispersion in the low-frequency region.

Other promising explanations for the observation of large dielectric constants are connected with the spontaneously arising interfaces. These are induced by the electronic phase separation or charge order as commonly observed in many transition-metal oxides. Though the true reason for the colossal polarization has not been completely clarified yet, it is possible that at least in some cases internal interfaces between the different phase-separated regions may play a role [36]. It is suggested that the dielectric behavior of these spontaneously forming heterogeneous regions represents a type of the long-known Maxwell-Wagner polarization effects, with the heterogeneity arising on a much finer scale close to the crystal unit cell. Here we suggest that this interpretation is associated with the following two aspects: (i) the density of charges arranges periodically in real space [see Fig. 5(b)]; however, whether such CCDW states of $1T$-TaS_2 can be considered as a particular form of heterogeneity and drive large polarizations is not clear at present; (ii) the domain wall configurations are on a scale of the unit cell and accordingly they would remarkably contribute to the dielectric properties of the system [17,33]. Therefore further investigations are necessary to clarify this issue.

C. The suppression of the dielectric constant by dc bias

The dielectric behavior we discussed here is attributed to BSPs that could be locally polarized, rather than to the free solitons that can transfer in long distances. In a weak applied dc electric field E, the bound soliton-antisoliton pair does not contribute to the dc transport due to its charge neutrality, but it does contribute to polarization [35,59].

The increase in the field strength suppresses the dielectric constant distinctly in the MHz frequency region; the relative dielectric constant ϵ_{r1} decreases from about 1.25×10^4 to 1.05×10^4 in the field of 10 V/cm at 2.0 MHz, as shown in Fig. 6(a). One may argue that under dc bias, the true temperature of the "heated" sample must be higher than the apparent temperature. Here we would clarify that E_B is moderate, and in contrast, stronger polarization is observed at higher temperatures [Fig. 6(b)]. Thus it is confirmed that the dielectric constant ϵ_{r1} decreases with the increasing of dc bias. Qualitatively, $\epsilon_{r1} \propto N\alpha$, where N is the number of dipoles per unit volume and α is the polarization coefficient. If N remains unchanged in the electric field, then α should decrease. Since α describes the local polarization, its decrease will not change the dc conductivity, in contrast with the experimental data.

Hence, N would decrease in an external dc bias field, consistent with the soliton tunneling model (Fig. 7). As the applied dc field increases, the potential barrier for the BSP activation decreases. For the solitons having positive charges,

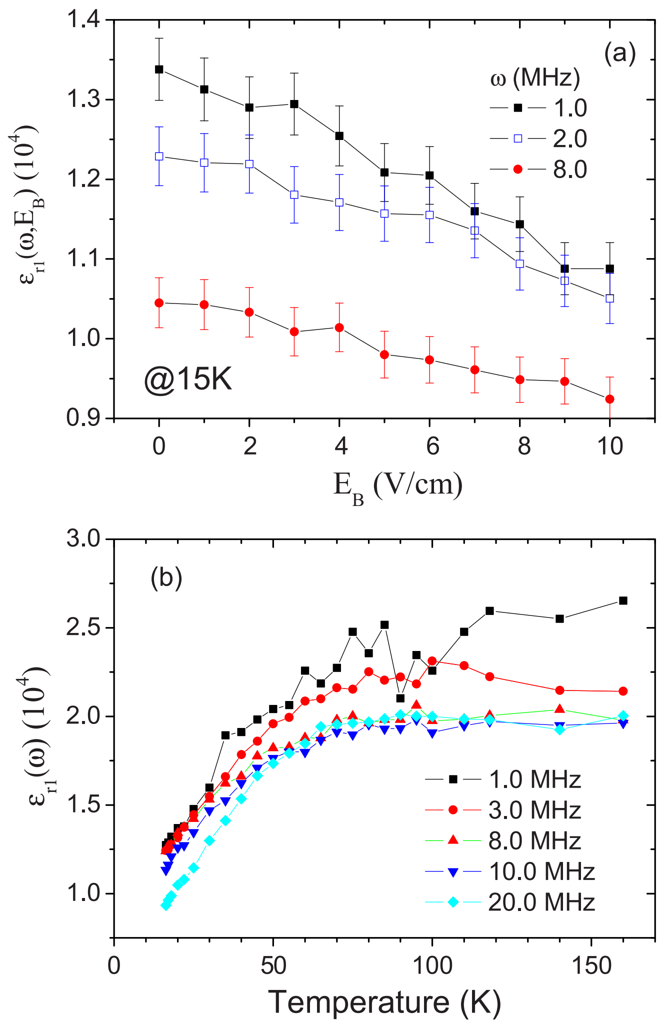

FIG. 6. (a) The dc-bias-dependent dielectric constant of $1T$-TaS_2 in the MHz region at $T = 15$ K. (b) The temperature-dependent $\epsilon_{r1}(\omega)$ at various MHz of $1T$-TaS_2 single-crystal samples.

the preferred direction of tunnelling would be along the external electric field, whereas the inverse applies for the negatively charged solitons, as shown in Fig. 7. Consequently, the probability of soliton tunneling is enhanced, inducing the suppression of polarization by dc bias.

The "grain and grain boundary" model should also be discussed in connection with the suppression of the dielectric constant in dc bias [63]. The model describes a reduction of the dielectric constant with increasing dc bias in ceramic systems. In such materials, double back-to-back Schottky potential barriers in micrometer scales are created at interfaces between grains due to charge trapping. Under a dc bias, the total width of the depletion region increases and then the dielectric constant should be suppressed [63]. However, in our experiment below $T = 50$ K, such polarization (often found at higher temperatures) should be frozen out and thus can be excluded.

D. The mechanisms of nonlinear conductance in the CCDW phase

Intrinsic nonlinearity unrelated to the CCDW ground state of $1T$-TaS_2 should be discussed. The two most common

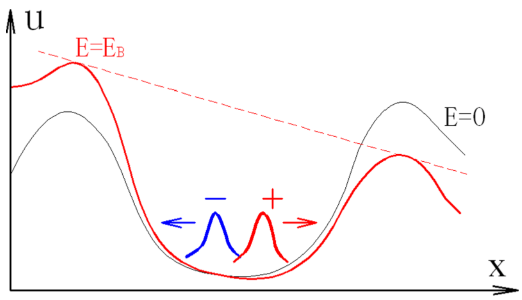

FIG. 7. The schematic pattern of a doublet, or a bound soliton-antisoliton pair (shown by bell-like curves, red for positively charged solitons and blue for negatively charged solitons), tunneling under dc bias. The label of the horizontal axis x presents the position of the real space, whereas for the vertical axis, u presents the potential energy. Note that the arrows represent the preference directions of the tunneling.

single-particle mechanisms are field ionization and impact ionization of charged impurities. To ionize impurity electrons with a binding energy of about 20 K by applying an electric field of about 10 V/cm would require that the impurity wave function extend over lengths of an order of 1.0 μm. It is possible, however, to generate extra carriers in weak electric fields if free carriers can be accelerated to sufficient kinetic energies to ionize bound electrons upon collision. This would require the mobility of carriers to be about 10^5 cm^2/(V $\cdot$ s). However, σ_{dc} at $T = 20$ K is about 2.5 $(\Omega \cdot \text{cm})^{-1}$ and the density of carriers is of the order of 10^{19}/cm^3 [16], thus the mobility is estimated to be only several cm^2/(V $\cdot$ s). Further, the experimental results from Ref. [28] also support a mobility of less than 20 cm^2/(V $\cdot$ s). Hence it is plausible to believe that the nonlinear conductivity is associated with the electrons' localization or the CCDW condensate.

The previous studies of $1T$-TaS_2 reported that in the presence of the nonlinear conductance the changes of the Hall coefficient could be neglected at $T = 4.2$ K [16]. Uchida *et al.* [16] proposed that the nonlinear conduction in $1T$-TaS_2 might be explained in terms of the collective excitations in pinned CDWs, if the creation of a soliton in pair with an antisoliton occurs in 2D CDW systems. Such excitations are expected to occur in the current temperature range as Rice *et al.* [56] proposed that the average number of φ-particle pairs $N(T) \propto \exp(-E_0/k_B T)$, where E_0 is the activation energy of solitons inside the Peierls gap. Therefore, the existence of BSPs' bearing with relatively small excitation energies would be more plausible as Rajaraman discussed [34] and the associated contribution to nonlinear conductivity may be understood. They cannot move freely without external excitations, as the applied dc field increases, and the potential barrier for both of the positively charged and negatively charged solitons would decrease [Fig. 5(b)], driving a nonlinear dc conductivity accompanied by the suppressed dielectric constant.

Vaskivskyi *et al.* [17] also observed the nonlinear CVCs and suggested that the unusual exponential curves can be understood within the model in terms of trapped carrier tunneling through barriers resulting from the transient domain wall structure. Nevertheless, as it becomes easier for the localized or trapped electrons to form delocalized charges in the presence of a dc field, the conductivity of the system is enhanced. However, we note that the CVCs in the CCDW state of $1T$-TaS_2 could not be fitted well by an exponential relation in the weak field range [17]. Thus the transport properties of $1T$-TaS_2 at low temperatures may be a complex issue. In combination with our experimental results on dielectric properties, a process which cannot be attributed to the hopping charge transport has been identified; thus we suggest that the collective excitations in the CCDW state of $1T$-TaS_2 cannot be neglected. In a recent report, Cho *et al.* [33] did observe two well-confined and nonmetallic in-gap states, located on the domain wall center and edges of neighboring domains. Further experiments are necessary to clarify whether the two in-gap states correspond to the two contributors: the localization states and the collective excitations (BSPs).

In Ref. [64], Rozhavsky *et al.* proposed a dynamic mechanism of topological charge creation in a commensurate 1D CDW near the contact with a normal metal and also predicted the presence of nonlinear conductivity. However, the associated feature of the CVC has a downward curvature in their model, which is inconsistent with our experimental data. To disclose the mechanisms of the nonlinear conductivity in 2D CDW systems is a complex issue; it is always a problem to distinguish the motion of solitons from other forms of nonuniform CDW excitations (e.g., creep), and thus more efforts are needed in future research work.

IV. SUMMARY

In summary, we have studied the in-plane electric-field-dependent charge dynamics in the in-plane of $1T$-TaS_2 single crystals in the CCDW phase. A large dielectric constant of $\sim 10^4$ exhibits up to 10^7 Hz, which is possibly due to the occurrence of bound soliton pairs or charge ordering of the system. The dielectric spectra disperse only slightly in our measured temperature and frequency range. We propose that besides the hopping carriers, the delocalization of BSPs may be another contributor to suppress $\epsilon_1(\omega)$ and the nonlinear conductivity with increasing of dc bias.

ACKNOWLEDGMENTS

The authors are very grateful for instructive discussions with Dong Wu and Nanlin Wang. The research work was supported by the National Science Foundation of China (Grant No. 10704054). Work at Brookhaven National Laboratory was supported by the US DOE under Contract No. DE-SC0012704.

[1] G. Gruner, Rev. Mod. Phys. **60**, 1129 (1988).
[2] P. Monceau, Adv. Phys. **61**, 325 (2012).
[3] C.-W. Chen, J. Choe, and E. Morosan, Rep. Prog. Phys. **79**, 084505 (2016).
[4] M. E. Itkis, F. Ya. Nad, and P. Monceau, J. Phys.: Condens. Matter **2**, 8327 (1990).
[5] J.-P. Pouget, Comptes Rendus Physique **17**, 332 (2016).
[6] F. Ya. Nad and P. Monceau, Phys. Rev. B **46**, 7413 (1992).

[7] G. Gruner, A. Zawadowski, and P. M. Chaikin, Phys. Rev. Lett. **46**, 511 (1981).
[8] I. G. Gorlova, S. G. Zybtsev, and V. Ya Pokrovskii, JETP Lett. **100**, 256 (2014).
[9] D. Staresinic, K. Biljakovic, W. Brutting, K. Hosseini, P. Monceau, H. Berger, and F. Levy, Phys. Rev. B **65**, 165109 (2002).
[10] D. Staresinic, P. Lunkenheimer, J. Hemberger, K. Biljakovic, and A. Loidl, Phys. Rev. Lett. **96**, 046402 (2006).
[11] M. E. Itkis, F. Ya. Nad, S. V. Zaitsev-Zotov, and F. Levy, Solid State Commun. **71**, 895 (1989).
[12] V. Nasretdinova and S. Zaitsev-Zotov, Physica B (Amsterdam, Neth.) **407**, 1874 (2012).
[13] F. J. Di Salvo, J. A. Wilson, B. G. Bagley, and J. V. Waszczak, Phys. Rev. B **12**, 2220 (1975).
[14] J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).
[15] A. A. Sinchenko, P. Lejay, and P. Monceau, Phys. Rev. B **85**, 241104(R) (2012).
[16] S. Uchida, K. Tanabe, and S. Tanaka, Solid State Commun. **27**, 637 (1978).
[17] I. Vaskivskyi, I. A. Mihailovic, S. Brazovskii, J. Gospodaric, T. Mertelj, D. Svetin, P. Sutar, and D. Mihailovic, Nat. Commun. **7**, 11442 (2016), and the Supplementary Information.
[18] J. Chang, E. Blackburn, A. T. Holmes, N. B. Christensen, J. Larsen, J. Mesot, R. Liang, D. A. Bonn, W. N. Hardy, A. Watenphul, M. V. Zimmermann, E. M. Forgan, and S. M. Hayden, Nat. Phys. **8**, 871 (2012).
[19] M. G. Velarde, W. Ebeling, and A. P. Chetverikov, C. R. Mec. **340**, 910 (2012).
[20] R. Comin, R. Sutarto, F. He, E. H. da Silva Neto, L. Chauviere, A. Frano, R. Liang, W. N. Hardy, D. A. Bonn, Y. Yoshida, H. Eisaki, A. J. Achkar, D. G. Hawthorn, B. Keimer, G. A. Sawatzky, and A. Damascelli, Nat. Mater. **14**, 796 (2015).
[21] M. Yoshida, R. Suzuki, Y. J. Zhang, M. Nakano, and Y. Iwasa, Sci. Adv. **1**, e1500606 (2015); M. Yoshida, T. Gokuden, R. Suzuki, M. Nakano, and Y. Iwasa, Phys. Rev. B **95**, 121405(R) (2017).
[22] M. J. Hollander, Y. Liu, W. J. Lu, L. J. Li, Y. P. Sun, J. A. Robinson, and S. Datta, Nano Lett. **15**, 1861 (2015).
[23] H. Mutka, L. Zuppiroli, P. Molinie, and J. C. Bourgoin, Phys. Rev. B **23**, 5030 (1981).
[24] A. Ubaldini and E. Giannini, J. Cryst. Growth **401**, 878 (2014).
[25] A. A. Sinchenko, P. Lejay, O. Leynaud, and P. Monceau, Phys. Rev. B **93**, 235141 (2016).
[26] Y. Huang, B. F. Hu, T. Dong, A. F. Fang, P. Zheng, and N. L. Wang, Phys. Rev. B **86**, 205123 (2012).
[27] F. J. Di Salvo and J. E. Graebner, Solid State Commun. **23**, 825 (1977).
[28] P. D. Hambourger and F. J. Di Salvo, Solid State Commun. **35**, 405 (1980).
[29] B. Dardel, M. Grioni, D. Malterre, P. Weibel, Y. Baer, and F. Levy, Phys. Rev. B **45**, 1462 (1992).
[30] J.-J. Kim, W. Yamaguchi, T. Hasegawa, and K. Kitazawa, Phys. Rev. Lett. **73**, 2103 (1994).
[31] L. Perfetti, P. A. Loukakos, M. Lisowski, U. Bovensiepen, H. Berger, S. Biermann, P. S. Cornaglia, A. Georges, and M. Wolf, Phys. Rev. Lett. **97**, 067402 (2006).
[32] B. Burk, R. E. Thomson, A. Zettl, and J. Clarke, Phys. Rev. Lett. **66**, 3040 (1991).
[33] D. Cho, G. Gye, J. Lee, S.-H. Lee, L. Wang, S.-W. Cheong, and H. W. Yeom, Nat. Commun. **8**, 392 (2017).
[34] R. Rajaraman, Phys. Rep. C **21**, 227 (1975).
[35] I. V. Krive and A. S. Rozhavsky, Solid State Commun. **55**, 691 (1985).
[36] P. Lunkenheimer, S. Krohns, S. Riegg, S. G. Ebbinghaus, A. Reller, and A. Loidl, Eur. Phys. J.: Spec. Top. **180**, 61 (2010).
[37] S. R. Elliott, Adv. Phys. **36**, 135 (1987).
[38] Y. C. Ma, C. Lu, X. Wang, X. Du, L. Li, and C. Petrovic, J. Phys.: Condens. Matter **28**, 395901 (2016).
[39] T. Ivek, T. Vuletic, S. Tomic, A. Akrap, H. Berger, and L. Forro, Phys. Rev. B. **78**, 035110 (2008).
[40] P. Lunkenheimer and A. Loidl, Phys. Rev. Lett. **91**, 207601 (2003).
[41] A. K. Jonscher, Nature (London) **267**, 673 (1977).
[42] R. J. Cava, R. M. Fleming, P. B. Littlewood, E. A. Rietman, L. F. Schneemeyer, and R. G. Dunn, Phys. Rev. B **30**, 3228 (1984).
[43] A. Fischer, P. Pahner, B. Lussem, K. Leo, R. Scholz, T. Koprucki, K. Gartner, and A. Glitzky, Phys. Rev. Lett. **110**, 126601 (2013).
[44] N. Croitoru and C. Popescu, Phys. Status Solidi A **3**, 1047 (1970).
[45] M. J. Cohen and A. J. Heeger, Phys. Rev. B **16**, 688 (1977).
[46] J. B. Balaguru Rayappan, S. A. Cecil Raj, and N. Lawrence, Physica B (Amsterdam, Neth.) **405**, 3172 (2010).
[47] A. V. Inyushkin, A. N. Taldenkov, and V. V. Florentiev, Synth. Met. **19**, 843 (1987).
[48] M. D. Nunnez-Regueiro, J. M. Lopez-Castillo, and C. Ayache, Phys. Rev. Lett. **55**, 1931 (1985).
[49] As thermal conductivity κ of $1T$-TaS_2 below $T = 100$ K is absent, the value κ of TaS_3 is taken as a reference. Moreover, the anisotropy of the thermal conductivity of $1T$-TaS_2 should be considered: it is acceptable that d/S and κ in the ab plane (cleaved surface) would be remarkably different from the case of the $\parallel c$ axis. For our measurement's configuration, the heat flow along the c axis is remarkable for the large ratio of contact area/thickness; hence at low frequencies the heating of the substrate as a whole contributes greatly to removing the Joule heating. That is, as most of the heating power flows into the sapphire substrate, the relaxation time τ_{SH} (of the sample and the substrate as a whole) is enhanced significantly. Thus the conductivity under dc bias mainly gives a chordal contribution. Nevertheless, the thermal relaxation effects could be neglected above 10 kHz, though systematic research work on the thermal properties of $1T$-TaS_2 is still necessary.
[50] P. B. Littlewood, Phys. Rev. B **36**, 3108 (1987).
[51] W.-y. Wu, L. Mihaly, and G. Gruner, Solid State Commun. **55**, 663 (1985).
[52] I. G. Austin and N. F. Mott, Adv. Phys. **18**, 41 (1969).
[53] N. Dean, J. C. Petersen, D. Fausti, R. I. Tobey, S. Kaiser, L. V. Gasparov, H. Berger, and A. Cavalleri, Phys. Rev. Lett. **106**, 016401 (2011).
[54] S. V. Zaitsev-Zotov and V. E. Minakova, Phys. Rev. Lett. **97**, 266404 (2006).
[55] S. Brazovskii, C. Brun, Z.-Z. Wang, and P. Monceau, Phys. Rev. Lett. **108**, 096801 (2012).
[56] M. J. Rice, A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Phys. Rev. Lett. **36**, 432 (1976).
[57] B. Horovitz and J. A. Krumhansl, Phys. Rev. B **29**, 2109 (1984).

[58] T. Matsuura, J. Hara, K. Inagaki, M. Tsubota, T. Hosokawa, and S. Tanda, Europhys. Lett. **109**, 27005 (2015).

[59] J. H. Miller, C. Ordonez, and E. Prodan, Phys. Rev. Lett. **84**, 1555 (2000).

[60] K. Inagaki, M. Tsubota, and S. Tanda, Phys. Rev. B **81**, 113101 (2010).

[61] A. Rojo-Bravo, V. L. R. Jacques, and D. Le Bolloch, Phys. Rev. B **94**, 201120 (2016).

[62] S. Krohns, P. Lunkenheimer, Ch. Kant, A. V. Pronin, H. B. Brom, A. A. Nugroho, M. Diantoro, and A. Loidl, Appl. Phys. Lett. **94**, 122903 (2009).

[63] T. B. Adams, D. C. Sinclair, and A. R. West, Phys. Rev. B **73**, 094124 (2006).

[64] A. S. Rozhavsky, Yu. V. Pershin, and A. S. Kovalev, Low Temp. Phys. **23**, 996 (1997).