Transition of a pristine Mott insulator to a correlated Fermi liquid: Pressure-dependent optical investigations of a quantum spin liquid

Weiwu Li,1 Andrej Pustogow,1 Reizo Kato,2 and Martin Dressel1
1Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, Stuttgart 70569, Germany
2RIKEN, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan

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Systematic pressure- and temperature-dependent infrared studies on the quasi-two-dimensional organic quantum spin liquid $\beta'$-EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ disclose the electronic and lattice evolution across the Mott insulator-metal transition. Increasing hydrostatic pressure continuously suppresses the insulating ground state; for $p > 0.6$ GPa, a Drude-like component develops indicating the appearance of coherent quasiparticles at the Fermi level. In the vicinity of the Mott transition, not only the electronic state changes rapidly, but also the vibration modes exhibit pronounced changes in frequency and Fano constant, underlining the strong coupling between lattice and electrons. The anisotropy of the in-plane optical response becomes inverted above 0.6 GPa. The findings are discussed in detail and summarized in a phase diagram comprising different experimental approaches.

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I. INTRODUCTION

The physics governing the Mott metal-insulator transition is of paramount importance for understanding strongly correlated electron systems. It is based on the concept that the electrons in a half-filled system, i.e., one charge per lattice site, tend to localize when electron-electron interactions become strong. From the viewpoint of the simple Hubbard model, the key parameter to control the metal-insulator transition is the ratio of Coulomb repulsion $U$ to bandwidth $W$. Despite enormous progress in dynamical mean-field theory (DMFT) [1,2] and decades of investigating typical Mott insulators, such as $V_2O_3$ [3–6], their ground state and the correlation-driven phase transition remain a challenge to condensed matter physicists because antiferromagnetic order, commonly observed in these compounds at low temperatures [4], obscures the genuine Mott state.

The solution is offered by quantum spin liquids, i.e., Mott insulators that do not exhibit any sign of long-range magnetic order despite strong antiferromagnetic coupling [7–10]. Several quasi-two-dimensional molecular crystals came under particular scrutiny as they form highly frustrated triangular arrangements of dimers occupied by a single charge with $S = \frac{1}{2}$. In $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ or $\beta'$-EtMe$_3$Sb[Pd(dmit)$_2$]$_2$, for instance, $J \approx 200$ K but no ordering occurs down to a few mK [9,11]. When temperature and correlations are scaled by the bandwidth, $T/W$ and $U/W$, a generic phase diagram of the Mott insulator-metal transition is unveiled: the quantum Widom line indicates the high-temperature crossover from bad metal to Mott insulator in the supercritical region above the first-order transition. Metallic quantum fluctuations were identified as a precursor of the Fermi liquid on the insulating side of the phase boundary, in close relation to its Pomeranchuk-like back bending [12]. However, not much is known about how the dynamics of charge carriers develops as correlations advance across the metal-insulator transition.

II. EXPERIMENTAL DETAILS

High quality single crystals of $\beta'$-EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ are prepared by an aerial oxidation method as described previously [14]; here EtMe$_3$Sb stands for ethyl-trimethyl-stibonium and dmit is 1,3-dithiole-4,5-dithiolate. As shown in Fig. 1(a) the organic conductor $\beta'$-EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ consists of alternating conducting layers of [Pd(dmit)$_2$]$_2$ dimers and insulating layers of EtMe$_3$Sb$^+$ cations. The quasi-two-dimensional electronic properties stem from the conduction band formed by the dominant $p$ orbital of the sulfur atom in [Pd(dmit)$_2$]$_2$. The bands of EtMe$_3$Sb are well below the Fermi level [15–18].
Specimens with shiny and flat surfaces are selected for optical measurements; the large size up to 0.5 mm allows measuring the low-energy response down to far-infrared frequencies. High-pressure experiments from \( p = 0.23 \)–1.2 GPa were conducted in a clamp-type BeCu cell [Fig. 1(b)] with Daphne 7373-type oil as pressure medium [19,20]. With the help of a home-built He-cryostat attached to a Fourier-transform spectrometer, temperature-dependent reflectivity measurements spanning from 150–8000 cm\(^{-1}\) were performed down to \( T = 10 \) K. The use of proper polarizers allow us to probe the response along different crystal directions. The optical conductivity is calculated via a Kramers-Kronig analysis with a Hagen-Rubens extrapolation for the metallic state and a constant low-frequency reflectivity in the insulating state [21].

III. RESULTS AND ANALYSIS

The temperature dependence of the optical properties measured with light polarized parallel to the \( a \) axis is presented in Fig. 2 for selected pressures below and above the critical pressure \( p_c \), defining the insulator-metal transition. A qualitatively similar temperature behavior is observed for \( E \parallel b \); the complete set of spectra is presented in the Supplemental Material [19]. Under ambient conditions the optical conductivity contains a pronounced mid-infrared absorption around 2000 cm\(^{-1}\) and a nonvanishing zero-frequency conductivity due to some incoherent bad metallic conductivity; a behavior rather typical for most families of organic metals [12,22]. The two strong and sharp vibrational modes observed around 1200 cm\(^{-1}\) are severely affected by electron-molecular vibrational coupling and have been extensively investigated by Yamamoto \textit{et al.} [23–25]. As the temperature is reduced, the low-frequency conductivity first rises slightly, but below 200 K it gradually vanishes as the Mott gap develops. The overall spectrum and temperature behavior does not change substantially when pressure increases up to \( p = 0.6 \) GPa.

From the false-color contour plots of the \( p = 0.23 \) and 1.2 GPa data, we see the qualitatively different behavior in the insulating and metallic regimes. For a quantitative analysis of the Drude-like contribution, the temperature dependence of the spectral weight \( SW = \int_0^{\infty} \sigma(\omega) d\omega \) is plotted in Figs. 2(g) and 2(h). In the insulating state the \( SW \) first rises upon lowering the temperature, but then it decreases as the Mott gap in the charge excitations gradually opens. This transition temperature is reduced with pressure, indicating a transition from an insulatorlike to a metallike behavior. Our conclusion is corroborated by pressure-dependent transport measurements [13], where the change in slope from \( d\rho/dT > 0 \) to \( d\rho/dT < 0 \) determines the crossover from metal to insulator. Above \( p_c = 0.6 \) GPa the spectral weight exhibits a completely different temperature behavior: the continuous increase down to \( T = 10 \) K is a measure for the build up of the coherent charge response. We do not see indications of a complete energy gap in our data, as inferred from the low-temperature upturn in the high-pressure resistivity [13]; future experiments at lower temperatures and smaller frequencies might clarify this controversy. It is interesting to note the recent results on a low-energy gap in the Dirac system \( \alpha-(\text{BEDT-TTF})_2\text{I}_3 \) where strong correlations eventually become effective [27,28].

In order to demonstrate the pressure dependence of the optical conductivity more clearly, in Fig. 3 we present the spectra...
recorded at \( T = 295, 150, \) and \( 10 \) K. At room temperature the mid-infrared absorption is barely affected by pressure, while the low-energy range increases slightly without developing a pronounced Drude peak; \( \beta'\)-EtMe\(_3\)Sb[Pd(dmit)\(_2\)]\(_2\) remains in a bad metallic state over the whole pressure range. Our findings are in accord with dc measurements \([13]\) indicating a decrease of resistivity within factor of ten as pressure increases to \(1.8\) GPa. The difference between low and high-pressure spectra becomes more pronounced when the sample is cooled down to \( T = 150 \) K, as shown in Fig. 3(b). In particular below \( 500 \) cm\(^{-1}\) the behavior clearly forks: a sharp Drude peak develops for \( p = 0.9 \) and \( 1.2 \) GPa, while the far-infrared conductivity is suppressed in the case of \( p = 0.23 \) GPa due to the gradual opening of the Mott gap upon cooling; this is reflected in the temperature behavior of the spectral weight, plotted in Fig. 2(b).

When going to the lowest temperature, thermally excited charge carriers freeze out completely; at \( T = 10 \) K a full gap has developed in the Mott state \((p_c < 0.6 \) GPa), while above \( p_c \) a Drude peak is present that becomes enhanced with increasing pressure. The corresponding spectral-weight transfer is quantitatively analyzed in the inset of Fig. 3(a), where the Drude term and mid-infrared band \( \int_{\omega_u}^{\omega_l} \sigma_1(\omega) d\omega \), (with the lower and upper bound \( \omega_l = 1000 \) cm\(^{-1}\) and \( \omega_u = 3000 \) cm\(^{-1}\), respectively) is plotted as a function of pressure. The small SW at low energies increases significantly only, when pressure exceeds \( p_c \) and the Mott gap has closed. Concomitantly the mid-infrared SW drops rapidly when the phase boundary is crossed. The transfer of SW over such a large energy scale is taken as evidence of strong correlations \([21,29]\).

Figure 3(d) illustrates that the change of optical conductivity at \( T = 10 \) K is most severe when pressure increases from \(0.53-0.6\) GPa. Here the Mott gap closes and the compound becomes metallic for higher pressure.

**IV. DISCUSSION**

A. Electron-electron interaction

In a next step we performed a Drude-Lorentz analysis of our spectra, in order to directly compare the results with theo-
In a first approximation it linearly decreases with pressure from the ambient pressure value \(2\Delta_0 = 650 \text{ cm}^{-1}\) [12] until it closes at \(p_c = 0.6 \text{ GPa}\), as shown in Fig. 4(c).

The degree of electronic correlations in the metallic state is commonly expressed by the effective mass \(m^*\), which can be estimated from the analysis of the spectral weight \(SW = \int \sigma(\omega) d\omega = \omega_p^2/8 = \pi n_e \omega_p^2/\pi^2 c^2\). Already the inset of Fig. 3(a) illustrates that the overall spectral weight is not recovered within the infrared range considered; this loss of \(SW\) with decreasing pressure evidences the enhancement of correlations. For a quantitative analysis we consider the ratio of the zero-frequency term \(\int \sigma_{\text{drude}}(\omega) d\omega\) related to the itinerant carriers and the intraband contribution obtained by subtracting the interband contributions from the total conductivity, \(SW_{\text{inter}} = SW_{\text{total}} - SW_{\text{intra}}\):

\[
\frac{m^*_\text{SW}}{m_b} = \frac{\int \sigma_{\text{intra}}^{\text{SW}}(\omega) d\omega}{\int \sigma_{\text{drude}}^{\text{SW}}(\omega) d\omega}.
\]  

\(SW_{\text{inter}}\) was accounted for by the high-frequency oscillator indicated in Figs. 4(a), 4(b) by the cyan color [19]. The development of \(m^*_\text{SW}/m_b\) with pressure is plotted in Fig. 4(d) as black squares.

Another approach starts from Fermi-liquid theory and considers the energy-dependent scattering rate and effective mass. From the extended Drude analysis of the complex optical conductivity \(\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)\) we obtain [21]

\[
\frac{m^*(\omega)}{m_b} = \frac{\omega_p^2}{4\pi \omega} \sigma_2(\omega) \frac{\omega_p^2}{4\pi \omega} \sigma_1(\omega) \frac{\sigma_1(\omega)}{\sigma_1^2(\omega) + \sigma_2^2(\omega)}.
\]

\[
\gamma(\omega) = \frac{\omega_p^2}{4\pi \omega} \sigma_2(\omega) \frac{\sigma_1(\omega)}{\sigma_1^2(\omega) + \sigma_2^2(\omega)}.
\]

where the plasma frequency \(\omega_p^2 = 8 \int_0^{\omega_c} \sigma_1(\omega) d\omega\) is calculated up to a cutoff \(\omega_c = 3000 \text{ cm}^{-1}\), chosen to disregard interband transitions. For \(T = 10 \text{ K}\), we plot the frequency dependence of the effective mass \(m^*(\omega)/m_b\) and scattering rate \(\gamma(\omega)\) for different pressures, \(p > p_c\), in Fig. 5. While at high energies the effective mass is basically energy independent, we see a prominent increase for frequencies below 600 cm\(^{-1}\). This dispersion becomes more pronounced as the Mott insulator transition is approached with lowering pressure. Correspondingly, the scattering rate \(\gamma(\omega)\) decreases as we go down in frequency, as displayed in Fig. 5(b). The quality of the data and the small frequency range do not allow us to draw quantitative conclusions on the functional dependence.

In Fig. 4(d) the effective mass is plotted as a function of pressure obtained from the spectral weight evaluation [Eq. (1)] and the \(\omega \to 0\) limit of the extended Drude analysis [Eq. (2)]. Both results are in good accord as far as the pressure dependence and the absolute value is concerned. When \(p\) increases on the metallic side, the system becomes less correlated and \(m^*/m_b\) decreases. The corresponding analysis of the \(E || b\) spectra yield a similar behavior. Our findings are also in accord with observations reported from optical investigations on \(\kappa\)-phase BEDT-TTF salts tuned by physical or chemical pressure [30,33–35]. As the systems approach the metal-to-insulator transition from the metallic side by enhancing electronic correlations, the effective mass increases rapidly.
B. Electron-phonon interaction

Ideally the Mott transition is supposed to represent a purely electronic phase transition; in a real crystal, however, an effect on the underlying lattice is unavoidable. Optical spectroscopy provides the unique tool to investigate the vibrational response of the molecular and crystal structure at the phase transition in order to extract information on changes in structure and charge distribution. The interplay of molecular vibrations and electronic states results in strong deviations from the Lorentzian shape of the $\alpha_g$ modes that are commonly described by the phenomenological Fano model \[36\]. The real part of the optical conductivity has the form:

$$\sigma_1(\omega) = \sigma_0 \frac{\Gamma \omega}{\Gamma^2 \omega^2 + (\omega - \omega_0)^2} + \frac{2q(\omega^2 - \omega_0^2)}{(\omega_0^2 - \omega^2)^2 + (\Gamma \omega)^2},$$

(4)

where $\sigma_0$ is the amplitude of the Fano contribution, $\Gamma$ the linewidth, and $q$ the dimensionless coupling parameter. Extremely strong coupling ($q = 0$) results in an antiresonance of Lorentzian shape, while for vanishing coupling ($1/q^2 \to 0$) we regain the standard Lorentz oscillator. When $q$ is positive $\sigma_1(\omega)$ has a minimum with negative values at low frequencies and a maximum at high frequencies. In the case of negative $q$, the shape is reversed: the minimum occurs at high and the maximum at low frequencies.

Figure 6 displays the behavior of the two strongest infrared-active $\alpha_g$ vibrational modes of $\beta'$-EtMe$_3$Sb[Pd(dmit)$_2$]$\_2$ as a function of temperature and pressure. The four $C=C$ bonds in the Pd(dmit)$_2$ unit vibrate in-phase within one molecule but out of phase with respect to the sibling molecule (C mode) within the [Pd(dmit)$_2$]$\_2$ dimer; the B mode denotes the out-of-phase vibration within the molecules as depicted in Fig. 6(a) \[23\]. Since the induced electric dipole within the dimer is perpendicular to the molecular axis, the C mode couples stronger to the electronic background than the B mode where the dipoles point along the Pd(dmit)$_2$ axes \[23–25\]. Due to thermal contraction, the vibrational features in general harden upon cooling; at the lowest pressure, however, the blue shift comes to a halt.
FIG. 7. (a), (b) Conductivity spectra of $\beta'$-EtMe$_3$Sb[Pd(dimit)$_2$]$_2$ recorded for two different polarizations, $E \parallel a$ and $E \parallel b$, at room temperature and $T = 10$ K. (a) For low pressure $p < p_c$ the anisotropy is conserved with temperature, (b) while a reversal at low frequencies is observed for $p > p_c$. (c) Temperature dependence of anisotropy ratio of the conductivity $\sigma_{ab}/\sigma_{aa}$ in the limit $\omega \to 0$ at various pressures. In the metallic state the extrapolated Haggen-Rubens values are used; for the insulating state we took just above the Mott gap since inside the gap the conductivity drops to almost zero. The dotted line indicates the isotropic case: $\sigma = \sigma_a$. (d) and (e) show the pressure dependent anisotropy of the spectral weight SW and conductivity($\omega \to 0$) for $T = 295$ and 10 K. The dashed line indicates the critical pressure $p_c = 0.6$ GPa of the Mott transition.

FIG. 8. Schematic pressure-temperature diagram of $\beta'$-EtMe$_3$Sb[Pd(dimit)$_2$]$_2$. The false-color contour plot is based on the optical conductivity along the $a$ axis in the limit $\omega \to 0$. The red squares refer to the change in the slope of the dc transport [13] where the temperature of the metal-insulator transition is defined by $d\rho/dT = 0$. The red circles indicate the temperatures, at which the activation energy changes; i.e., the maximum of $d\ln\rho/d(1/T)$. From our optical experiments we analyze the temperature dependence of the vibration features and shift in spectral weight. The black circles correspond to the maxima of the $C$-mode frequency plotted in Fig. 6(g). The black squares refer to the temperatures where the low-frequency spectral weight is largest, as plotted in Fig. 2. The green triangles represent the temperatures, when the ratio of $\sigma_{ab}/\sigma_{aa}$ crosses unity. The upper scale is extracted from Fig. 4(e). See Supplemental Material [19] for more details.

At the Mott transition, similar to previous investigations at $p = 0$ [18], and even softens slightly; concomitantly, the Fano shape becomes more pronounced [Figs. 6(c)–6(h)]. This behavior clearly reflects the spectral weight redistribution upon formation of the Mott gap at lower frequencies, which modifies the electronic background at the vibration frequency. While the mode is sitting on the low-energy side of optical Hubbard excitations in the insulating state, where it couples to a highly polarizable background, the spectral weight transfer to lower frequencies at larger $T$ and $p$ involves the onset of screening.

The low-temperature spectra exhibit a clear change in resonance frequency $\omega_0$ and electronic coupling $g$ when the pressure drops below $p_c$, as depicted in Figs. 6(j), 6(k). It is interesting to note that dilatometric measurements on the related compound $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl also reveal an abrupt length reduction when tuned by pressure across the first-order insulator-metal line [37]. In the same way, our observations infer that the insulator has a bigger volume (small $\omega_0$) than the conductive phase (large $\omega_0$); obviously, pressure favors the state with smaller volume.

Our optical investigations of the electronic response clearly show a shift of spectral weight from localized to itinerant charge carriers, i.e., interdimer excitations become stronger on the expense of the intradimer excitations. This is also reflected in vibrational features. The mode shifts up in frequency as pressure increases above the Mott transition. On the other hand we find the Fano coupling constant $1/q^2$ vanishing at $p_c = 0.6$ GPa as the vibrational features become simple Lorentzians. This implies that above $p_c$ the modes become decoupled from the electronic background, which has turned from polarizable to screening.

### C. Electronic anisotropy

$\beta'$-EtMe$_3$Sb[Pd(dimit)$_2$]$_2$ is a quasi-two-dimensional conductor with a small in-plane anisotropy at ambient conditions: $\sigma_{aa} > \sigma_{ab}$. While the ratio $\sigma_{ab}/\sigma_{aa} = 0.8$–0.9 remains constant throughout the insulating state ($p < p_c$), the Drude term is found to increase more rapidly for $E \parallel b$ than for $E \parallel a$ when entering the metallic phase. In Fig. 7 we present the temperature and pressure dependence of the anisotropy $\sigma_{ab}/\sigma_{aa}$, as obtained from the $\omega \to 0$ data indicating the inversion for low temperature and high pressure. Similar results are obtained from the analysis of the spectral weight of the Drude term in both directions. Our findings infer the opening of a pseudogap along the $a$ axis. Beside investigations of the thermal expansion, we suggest more detailed studies of the Fermi surface of $\beta'$-EtMe$_3$Sb[Pd(dimit)$_2$]$_2$ for high pressure and low temperature where the Mott phase transition is crossed and the system turns from an insulator to a metal.

There is another aspect that would level the anisotropy but might influence the phase transition. Recent Hall studies
on the $\kappa$-salt spin-liquid Mott insulators $\kappa$-(BEDT-TTF)$_2$$X$ [$X = \text{Cu}_2(\text{CN})_3$, $\text{Ag}_2(\text{CN})_3$, and $\text{B}(\text{CN})_4$] yield evidence for Mott-Anderson localization [38,39]. It would be of interest to extend these Hall investigations to the title compound $\beta'$-EtMe$_3\text{Sb}[\text{Pd}(\text{dimt})_2]_2$. How generic are the observations and to what extent can defects affect the Mott transition in the title compound?

V. SUMMARY AND CONCLUSIONS

Employing temperature- and pressure-dependent optical investigations on the quantum-spin-liquid candidate $\beta'$-EtMe$_3\text{Sb}[\text{Pd}(\text{dimt})_2]_2$, we could elucidate the electrodynamics at the Mott insulator-metal transition in detail. The results unambiguously confirm the realization of the pure bandwidth-controlled phase transition via applied pressure. From our optical data we can determine values for the on-site Coulomb repulsion $U$ and the bandwidth $W$. With increasing pressure the effective correlations $U/W$ are continuously reduced. The extracted parameters of $T/W$ and $U/W$ are in good agreement with DMFT calculations [19] and recent optical studies [12].

In the pressure-temperature phase diagram of Fig. 8 we summarize our optical experiments and complement them with transport data [13]. At ambient pressure $\beta'$-EtMe$_3\text{Sb}[\text{Pd}(\text{dimt})_2]_2$ is a Mott insulator with a Mott-Hubbard gap of 650 cm$^{-1}$ that decreases with pressure and vanishes at $p_c = 0.6$ GPa. The high-temperature electronic state can be characterized as a rather poor metallic state with only a small amount of free charge carriers. When cooled down at ambient and weak pressure ($p < p_c$), the system becomes insulating below the quantum Widom line, i.e., the spectral weight shifts to higher energies as the Mott gap opens in the optical spectrum. Due to electron-molecular vibrational coupling, we also identify changes in the vibrational features (Fig. 6). With $p > p_c$ a metallic ground state is established at reduced temperatures with a pronounced zero-frequency component. When the Mott transition is approached from the metallic side, the increase of correlation strength is monitored quantitatively by the enhancement of the effective mass $m^*$ towards $p_c$. Lower-temperature measurements are required for a more detailed characterization of this potential Fermi-liquid state.

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[19] In the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.99.115137 we plot the raw data of the measured reflectivity spectra at all temperatures, pressure values, and both polarizations, $E \parallel a$ and $E \parallel b$. Also shown is the low-temperature conductivity at different pressure values together with the corresponding Drude-Lorentz fits used to extract the Coulomb correlation $U$ and bandwidth $W$ in the insulating cases. For the metallic cases, the spectral weight of the Drude and intraband contributions are shown.