

## Subgap optical absorption induced by quantum lattice fluctuations at the Peierls edge in PtCl chain complexes

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The temperature dependence of the low-energy tail of the interband optical absorption band at the Peierls edge has been studied in halogen-bridged linear-chain complexes,  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$  and  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$ , en being ethylenediamine. The absorption spectrum and its temperature dependence are explained well in terms of the subgap density of states of the one-dimensional electronic bands induced by the quantum vibration of Cl ions of the breathing mode. Both substances are found to have a dimensionless electron-phonon coupling constant of  $\lambda \approx 1.2$ , the zero-temperature gap parameter of  $\Delta_0 \approx 1.45$  eV, and the transfer integral of  $t_0 \approx 0.4$  eV. Because of the strong electron-phonon coupling the temperature dependence of the energy gap is dominated by the self-energy effect; even at 0 K the self-energy amounts to 0.07–0.08 eV, being considerably greater than the self-energies in usual semiconductors. The role of the anharmonicity of the chainlike Pt-Cl bonds is discussed in relation to the origin of the large gap parameter. [S0163-1829(96)05627-5]

### I. INTRODUCTION

Halogen-bridged transition-metal chain complexes, so-called *MX* chain complexes, have emerged as an important class of one-dimensional (1D) electronic materials with strong electron-phonon coupling and electron correlation. In light of one-band<sup>1-3</sup> and two-band<sup>4-6</sup> extended Peierls-Hubbard models and the recently developed Su-Schrieffer-Heeger-type models<sup>7-9</sup> quantitative knowledge of the electron-phonon coupling involved in the valence-alternating chainlike bonds, that is, the charge-density-wave (CDW) state, is essential for understanding the electronic properties of the *MX* chain complexes. However, the extreme anharmonicity of the chain lattice, as well as a significant hybridization between the transition-metal  $d_{z^2}$  and low-lying halogen  $p_z$  orbitals, makes the electronic processes quite complicated in comparison to the case of conjugated polymers such as *trans*-polyacetylene.

It has been widely recognized that the energy gap of the CDW phase of an *MX* chain complex is determined by the coupling of valence electrons of the constituent metal ions (platinum or palladium) with the in-chain displacement of halogen ions. Optical transition at this Peierls gap manifests itself as a prominent feature in the reflection spectrum in the near-infrared or visible region depending on the substances.<sup>10-14</sup> If one attempts to measure the absorption spectrum of this interband transition by the transmission method it is difficult to gain access to the peak position because the absorbance rises up steeply from a region of photon energy far below the peak position.<sup>4,10,15-25</sup> On account of its large bandwidth and large oscillator strength the observed absorption edge has been conceived as the tail end of the absorption band.<sup>4,15,21-25</sup> Interestingly the spectral position of this absorption edge has a pronounced temperature

dependence;<sup>10,19,21</sup> besides, the temperature dependence is significantly greater than that of the energy gap in usual semiconductors. Although this phenomenon seems to reveal unique properties of the electron-phonon coupling in the *MX* chain complexes, to our knowledge, the details have not been studied to date.

It has turned out recently that the quantum fluctuations of lattice<sup>26-28</sup> and kinks<sup>24,29</sup> strongly influence the line shape of the interband and midgap absorption bands, respectively, in 1D Peierls systems including *MX* chain complexes. McKenzie and Wilkins<sup>26</sup> have argued the roles of the quantum and thermal lattice fluctuations due to a homopolar optical phonon with wave vector of  $2k_F$ . They have shown that the lattice fluctuations induce a nonvanishing density of states inside the forbidden gap, and thus the interband optical absorption band extends widely below the fundamental absorption edge. Subsequently Kim, McKenzie, and Wilkins<sup>27</sup> have developed a method for numerically calculating the optical conductivity spectrum under the influence of the lattice disorder including lattice vibrations. According to their calculation the spectrum of the "subgap" optical conductivity has a universal scaling form. In fact it has successfully explained the temperature-dependent line shape of the broad interband absorption spectra in a variety of 1D Peierls systems such as KCP(Br), *trans*-polyacetylene, and blue-bronze,<sup>27,28</sup> which belong to the strong, intermediate, and weak regimes, respectively, of the electron-lattice coupling strength. The theory has been applied further to the excitation spectrum for the exciton photoluminescence in an *MX* chain complex  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$ , en denotes ethylenediamine.<sup>30,31</sup> The result clearly proves the presence of the subgap tail of the density of states in the *MX* chain complex as well. Since the excitation spectrum, however, does not give the absorption spectrum itself there remain considerable un-

certainties in the important issues such as the identification of the phonon mode responsible for the electron-phonon coupling.

In the present paper, we perform a direct measurement of the subgap optical absorption in two PtCl-chain complexes  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$  and  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$  in a temperature range of 10–300 K. The former (hereafter referred to as  $\text{ClO}_4$  salt) has been studied extensively so far and is known to have the strongest CDW of many  $MX$  chain complexes,<sup>9,32</sup> while at room temperature the latter (hereafter referred to as  $\text{BF}_4$  salt) is isomorphous with the orthorhombic phase of the  $\text{ClO}_4$  salt<sup>14</sup> and has recently been found to resemble the  $\text{ClO}_4$  salt well in various aspects of optical properties.<sup>14,25,33</sup> The experimental results are quantitatively analyzed in terms of the above-mentioned Kim-McKenzie-Wilkins theory to investigate what kind of phonon mode dominates how strongly the electron-phonon coupling in the two substances. Basic properties of the CDW state of the Pt-Cl chain bonds are discussed on the basis of the knowledge obtained from this analysis.

## II. EXPERIMENT

Single crystals are grown by the evaporation method from the aqueous solution of chemically synthesized materials. The 50–80- $\mu\text{m}$ -thick crystals are used as the samples. The temperature of the sample is controlled with a continuous flow cryostat (Oxford Instruments CF1204) and a temperature controller (Oxford Instruments ITC4). The optical absorption spectrum is measured using an optical multichannel system. A tungsten-halogen lamp is used as the light source. Light of wavelength longer than 520 nm is obtained with a glass filter and is polarized parallel to the Pt-Cl chain axis of the crystal with a Glan-Thompson prism. The light transmitted by the sample is dispersed with a polychromator (Ritu Applied Optic MC-30ND). The dispersed light is detected by a charge-coupled-device (CCD) camera (Photometrics PM512). The shutter of the CCD camera is synchronized with the shutter of the light source. The intensity of the light source and the exposure time are set as low as possible. The typical exposure time chosen to take an absorption spectrum is 0.2 s.

## III. RESULTS AND ANALYSIS

Figures 1(a) and 1(b) show the absorption spectra of the  $\text{ClO}_4$  and  $\text{BF}_4$  salts, respectively, at several temperatures between 100 and 300 K. The thickness of the sample of the  $\text{ClO}_4$  and  $\text{BF}_4$  salt is 80 and 70  $\mu\text{m}$ , respectively. The fundamental optical transition is known to take place around 2.8 eV in the reflection spectrum in both  $\text{BF}_4$  and  $\text{ClO}_4$  salts.<sup>10–14</sup> Nevertheless in the present transmission measurement the intrinsic absorption starts to rise around 2.0 eV, and rapidly attains the instrumental limit, which is determined by the degree of the linear polarization of the light source; the weak absorption band seen around 1.6 eV in Fig. 1(b) is due to the extrinsic midgap states.<sup>25,33</sup> In Fig. 2 is plotted, as a function of temperature, the photon energy, say  $\hbar\omega_0$ , at which the absorbance equals 2.0. The absorption band shifts continuously toward higher energy as temperature decreases.

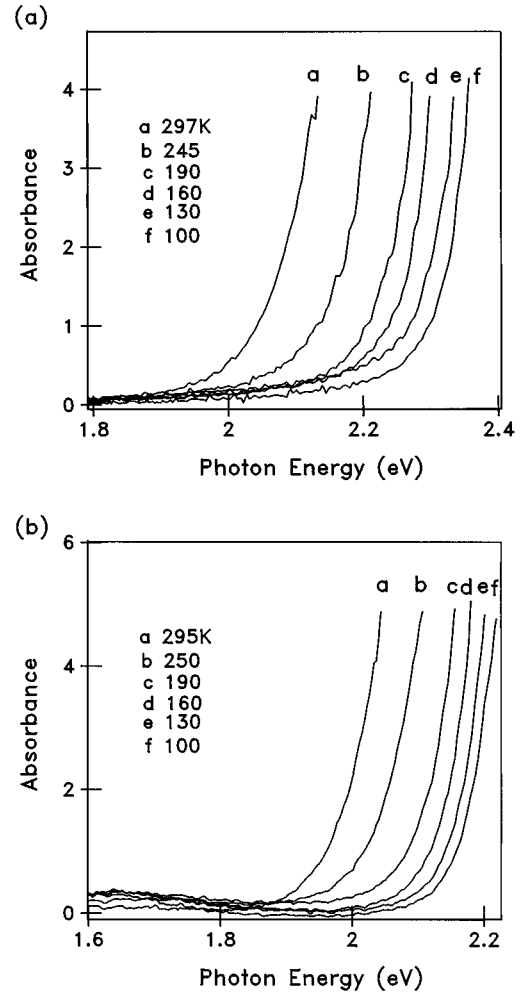


FIG. 1. Absorption spectrum in (a)  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$  and (b)  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$  at several temperatures. The electric field of light is polarized parallel to the chain axis.

In the  $\text{BF}_4$  salt a discontinuous increase of  $\hbar\omega_0$  by about 30 meV takes place around 255 K with a hysteresis of about 3 K, indicating the occurrence of a structural modification similar to the case of the  $\text{ClO}_4$  salt.<sup>21</sup> The present study deals with the low-temperature phase. In both salts the shift almost levels off below 100 K, showing that optical phonons with energies appreciably higher than 10 meV play a major role in determining the temperature dependence of the absorption tail.

It has been demonstrated by the studies on the resonance Raman scattering<sup>34,35</sup> that the breathing mode of Cl ions couples very strongly with electrons of the conduction and valence bands. The Kim-McKenzie-Wilkins theory cited in Sec. I argues that if such a homopolar and dispersionless optical phonon of frequency  $\omega_p$  dominates the electron-phonon coupling in a 1D system the properties of the subgap states are determined by the disorder parameter

$$\eta = \eta_0 \coth\left(\frac{\hbar\omega_p}{2kT}\right), \quad \eta_0 = \frac{\pi\hbar\omega_p\lambda}{2\Delta}, \quad (1)$$

where  $\lambda$  is the dimensionless electron-phonon coupling constant,  $\Delta$  is the gap parameter,  $k$  is the Boltzmann constant,

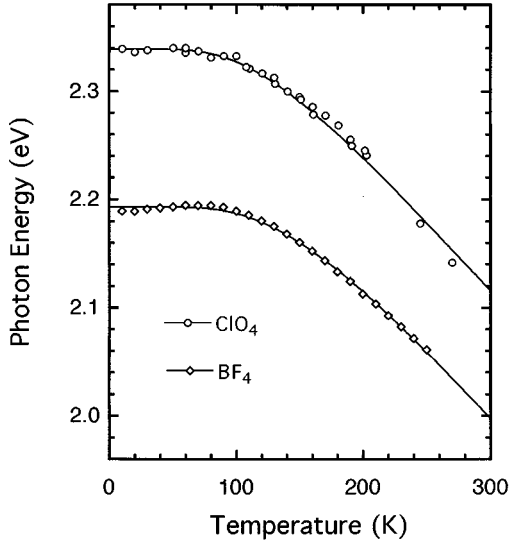


FIG. 2. Temperature dependence of the spectral position of the absorption edge in (○)  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$  and (◇)  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$ . The solid lines are the least-squares fits of Eq. (6) to the experimental data.

and  $T$  is temperature. In the following the present results are analyzed on the basis of this Kim-McKenzie-Wilkins theory.

The lattice disorder due to the quantum and thermal lattice motions eliminates the inverse-square-root singularity of the joint density of states, which occurs in ideal 1D systems, to induce the subgap states. The important point of the work of Kim, McKenzie, and Wilkins is the finding that the resultant optical-conductivity spectrum  $\sigma(\omega)$  below the peak position  $\omega_{\text{peak}}$  has a universal form, which is fitted with the function

$$\sigma(\omega) = \sigma_{\text{peak}} \exp \left\{ -0.49 \left| \frac{\omega_{\text{peak}} - \omega}{\Gamma} \right|^2 - 0.20 \left| \frac{\omega_{\text{peak}} - \omega}{\Gamma} \right|^3 \right\}, \quad (2)$$

where  $\Gamma$  is the half width for the low-energy side of the peak; furthermore, the ratio  $\Gamma/\omega_{\text{peak}}$  scales with  $\eta$  as

$$\frac{\Gamma(\eta)}{\omega_{\text{peak}}(\eta)} = 0.414\eta^{0.62} + 0.077\eta^{1.62}. \quad (3)$$

Wada and Yamashita<sup>13</sup> have evaluated the real and imaginary parts of the dielectric function in the  $\text{ClO}_4$  salt by the Kramers-Kronig analysis of the reflectivity spectrum measured at 77 K. In Fig. 3 the conductivity spectrum  $\sigma(\omega) = \omega \varepsilon''(\omega)/4\pi$ , where  $\varepsilon''(\omega)$  is the imaginary part of the dielectric function, obtained from their data is compared with the conductivity spectrum at 80 K obtained from the present transmission experiment.<sup>36</sup> It appears that the present transmission experiment deals with the spectral region where  $\sigma(\omega)$  is 3 orders of magnitude smaller than that around the peak. In Fig. 3 is also shown a theoretical curve calculated from Eq. (2) with  $\hbar\omega_{\text{peak}} = 2.78$  eV and  $\hbar\Gamma = 0.155$  eV. Note that for  $\omega \leq \omega_{\text{peak}}$  the single theoretical curve reproduces the two contrasting and independent data very well. It may be

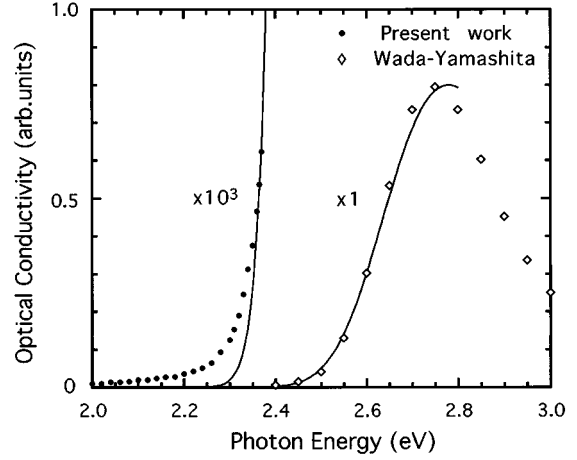


FIG. 3. Optical conductivity spectrum obtained from (●) the present transmission experiment and (◇) the reflection experiment (Ref. 13) in  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$  at 80 and 77 K, respectively. The numerical label of the ordinate corresponds approximately to the absorption coefficient in the unit of  $10^6 \text{ cm}^{-1}$ . The solid line is the theoretical curve calculated from Eq. (2). Note that for photon energies below 2.4 eV the scale of the ordinate is magnified by  $10^3$  times relative to the scale above 2.4 eV.

concluded, therefore, that Eq. (2) is appropriate to describe the fundamental absorption band over a wide spectral region below  $\omega_{\text{peak}}$ .

The photon energy  $\hbar\omega_0$  plotted in Fig. 2 is the spectral position at which the absorption coefficient takes a constant value of  $\sim 3 \times 10^2 \text{ cm}^{-1}$ . Its thermal shift arises from the thermal changes in  $\omega_{\text{peak}}$  and  $\Gamma$ . Since, as  $\eta$  changes, the exponential term on the right-hand side of Eq. (2) varies much faster than  $\sigma_{\text{peak}}$ , the frequency  $\omega_0$  is expected to follow the changes in  $\omega_{\text{peak}}$  and  $\Gamma$  while satisfying the relationship

$$\frac{\omega_{\text{peak}}(\eta) - \omega_0(\eta)}{\Gamma(\eta)} = \chi = \text{const.} \quad (4)$$

We have  $\hbar\omega_0 = 2.34$  eV for the  $\text{ClO}_4$  salt at 80 K. Then from the above-mentioned values of  $\omega_{\text{peak}}$  and  $\Gamma$  at 77–80 K the constant  $\chi$  should be  $\sim 2.8$ . The analytical formula for  $\omega_{\text{peak}}$  is unavailable as a function of  $\eta$ . However, the numerical calculation of Kim, McKenzie, and Wilkins<sup>27</sup> suggests that  $\hbar\omega_{\text{peak}}$  decreases almost linearly with increasing  $\eta$  at a rate of  $\sim 0.2\eta\Delta$ . In addition Abrikosov and Dorotheyev<sup>37</sup> have shown that the gap parameter  $\Delta$  itself decreases with increasing lattice disorder at a rate of  $\sim \pi\eta\Delta/8 \approx 0.4\eta\Delta$ . Consequently within the framework of the Kim-McKenzie-Wilkins theory it may be reasonable to write

$$\hbar\omega_{\text{peak}}(\eta) = 2\Delta_0(1 - 0.5\eta), \quad (5)$$

with the zero-temperature gap parameter  $\Delta_0$ . Then substitution of Eqs. (3) and (5) into Eq. (4) yields

$$\hbar\omega_0(\eta) = 2\Delta_0(1 - 0.5\eta) \{1 - \chi(0.414\eta^{0.62} + 0.077\eta^{1.62})\}. \quad (6)$$

TABLE I. The zero-temperature gap parameter  $2\Delta_0$ , the phonon energy  $\hbar\omega_p$ , the zero-temperature dimensionless disorder parameter  $\eta_0$ , the spectral position parameter  $\chi$ , and the dimensionless electron-phonon coupling constant  $\lambda$  in the  $\text{ClO}_4$  and  $\text{BF}_4$  salts.

Substance	$2\Delta_0$ (eV)	$\hbar\omega_p$ (meV)	$\eta_0$	$\chi$	$\lambda$
$\text{ClO}_4$ salt	2.90	35.8	0.048	2.7	1.21
$\text{BF}_4$ salt	2.89	43.2	0.056	3.1	1.16

Now let us attempt to evaluate the parameters  $2\Delta_0$ ,  $\eta_0$ ,  $\chi$ , and  $\omega_p$  by the least-squares fit of Eq. (6) to the experimental data shown in Fig. 2. As shown in Fig. 2, the experimental results can be reproduced very well by Eq. (6). Table I lists the values of the parameters thus obtained for two substances. It is found from this analysis that upon an increase of temperature from 0 to 250 K the disorder parameter  $\eta$  changes from 0.048 to 0.071 in the  $\text{ClO}_4$  salt and from 0.056 to 0.073 in the  $\text{BF}_4$  salt. According to the numerical calculation by Kim, McKenzie, and Wilkins<sup>27</sup> an increase in  $\eta$  leads to a decrease in  $\sigma_{\text{peak}}$ . In the present case the amount of decrease in  $\sigma_{\text{peak}}$  due to the increase in  $\eta$  can be estimated to be only about 5% or less, justifying the assumption that the dependence of  $\sigma_{\text{peak}}$  on  $\eta$  is negligible in deriving Eq. (4).

The parameters  $2\Delta_0$  and  $\eta_0$  give  $\hbar\omega_{\text{peak}} = 2\Delta_0(1 - 0.5\eta_0) = 2.83$  eV for the  $\text{ClO}_4$  salt at 0 K, in good agreement with the result of the reflectivity experiment by Wada and Yamashita at 77 K despite that the least-squares-fit analysis has been made by using only the transmission data. The values of  $\chi$  of 2.7(3.1) for the  $\text{ClO}_4(\text{BF}_4)$  salt are also quite reasonable. In the  $\text{BF}_4$  salt, therefore, the absorption band is expected to have its peak around 2.8 eV as well.

Another quantity that should be tested by the independent experiment is the phonon energy  $\hbar\omega_p$ : The energies 35.8 (43.2) meV obtained for the  $\text{ClO}_4$  ( $\text{BF}_4$ ) salt agree with the Raman energy 38.5 meV of the breathing mode of Cl ions within the error  $\pm 5$  meV of the least-squares fit. This result proves that the breathing mode of Cl ions plays a dominant role in the electron-phonon coupling processes in the CDW phase, as expected from the resonance Raman data.

Long *et al.*<sup>30,31</sup> have obtained the values of  $2\Delta_0$ ,  $\eta_0$ , and  $\hbar\omega_p$  for the  $\text{ClO}_4$  salt, which differ significantly from the

values obtained by the present study. The discrepancies may be ascribed to their use of the excitation spectrum of photoluminescence instead of the absorption spectrum itself.

#### IV. DISCUSSION

Results of the present absorption experiment are summarized in the following two matters: First, the Kim-McKenzie-Wilkins theory has enabled us to separate the observed thermal shift of the absorption band into two components arising from  $\omega_{\text{peak}}$  and  $\Gamma$ . We have  $\eta\Delta_0 = 0.070$  (0.081) eV at 0 K and 0.104 (0.107) eV at 250 K for the  $\text{ClO}_4$  ( $\text{BF}_4$ ) salt. [Hereafter the terms ‘‘ $\text{ClO}_4$  ( $\text{BF}_4$ ) salt’’ specifying the substances for the numerical factors quoted are abbreviated unless otherwise noted.] This means that at 250 K, for instance, about 20% of the observed shift of  $\omega_0$  comes from the temperature dependence of  $\omega_{\text{peak}}$ , and the rest comes from  $\Gamma$ . Secondly, a reliable value of the dimensionless electron-phonon coupling constant  $\lambda$  can be derived, as shown in Table I, in the  $MX$  chain complexes. Here the basic properties of the CDW state of the  $\text{ClO}_4$  and  $\text{BF}_4$  salts are discussed on the basis of these results.

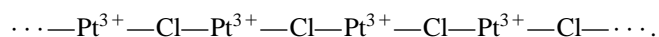
##### A. Temperature dependence of energy gap

The mechanism of the temperature dependence of the energy gap is an important subject of semiconductor physics.<sup>38</sup> The present results suggest strongly that the thermal shift of the Peierls gap in the PtCl-chain complexes is dominated by the self-energy effect. In this context it may be worth recalling that the thermal shift of the energy gap in layered III-VI semiconductors is induced by the self-energy effect due to a homopolar optical phonon.<sup>38,39</sup> The key to this phenomenon is the presence of a highly symmetric phonon mode in addition to an extreme anisotropy of chemical bond.<sup>40</sup> The homopolar optical phonon responsible for the self-energy in those layered semiconductors is the fully symmetric normal mode, which modulates the thickness of layers while keeping the bisectric planes of all layers at rest. The deformation potential of the energy gap due to this mode is essentially large because only a little energetic cancellation occurs between the expansion (compression) of the interlayer van der Waals bond and the concomitant compression (expansion) of the intralayer covalent bond.

Low dimensionality is more distinctive in  $MX$  chain complexes. Each chain of a PtCl complex consists of valence alternating bonds, which can be depicted as



with  $\rho < 1$ . The intervening Cl ions are symmetrically displaced toward  $\text{Pt}^{(3+\rho)+}$  ions by about 0.4 Å from the central position between  $\text{Pt}^{(3-\rho)+}$  and  $\text{Pt}^{(3+\rho)+}$ . This structure results from the Peierls instability of the metallic chain<sup>41</sup>



Clearly, the instability is driven by the  $2k_F$  phonon mode of Cl ions, in which every Cl ion vibrates out of phase against the Cl ion on the next site. The dimerization of Cl ions accompanies the transfer of a charge  $\rho e$  between adjacent  $\text{Pt}^{3+}$  ions to induce a wide energy gap of  $2\Delta_0 \sim 3$  eV between the  $d_{z^2}$ -like orbitals of the resultant  $\text{Pt}^{(3-\rho)+}$  and  $\text{Pt}^{(3+\rho)+}$  ions. Since the breathing mode of the CDW state

corresponds in symmetry to the  $2k_F$  mode of the metallic phase, it would directly modulate the charge  $\rho e$  and thus would exert a strong perturbation on the energies of the valence and conduction bands. This situation is manifested by the above-mentioned large values of  $\eta\Delta_0 = 0.070(0.081)$  eV at 0 K, which are the self-energies at 0 K of the renormalization of the energy gap by the electron-breathing-mode coupling. In fact they are considerably greater than the self-energy, 0.03 eV, at 0 K in layered III-VI semiconductors.<sup>38</sup>

### B. Dimensionless electron-phonon coupling constant and gap parameter

The subgap absorption, as well as the self-energy of the gap, reflects the strength of the electron-breathing-mode coupling. Substitution of the values of  $\eta_0$ ,  $\hbar\omega_p$ , and  $\Delta_0$  into Eq. (1) yields  $\lambda = 1.21(1.16)$ , confirming that the present substances belong to the strong-coupling regime. The values of  $\lambda$  are comparable to the case,  $\lambda = 0.96$ ,<sup>27</sup> of KCP(Br) and are greater by a factor of 2–3 than the value in *trans*-polyacetylene.<sup>27,42</sup>

In the strong-coupling regime,  $\lambda$  can be connected approximately to the transfer integral  $t_0$  between Pt ions by a relationship  $\lambda^{-1} = \pi t_0 / \Delta_0$ .<sup>43,44</sup> It follows from the values of  $\lambda$  that  $t_0 / \Delta_0 \approx 1 / (\pi\lambda) = 0.26(0.28)$  and thus  $t_0 \approx 0.38(0.40)$  eV. This result is compared to  $t_0 = 0.3$  eV obtained from a tight-binding band calculation by Whangbo and Foshee<sup>45</sup> and 0.67 eV estimated by Baeriswyl and Bishop<sup>46</sup> on the basis of the interband oscillator strength. The value of  $t_0 / \Delta_0$  is a measure of the strength of CDW. In the strong-coupling regime the disproportionation  $\rho$  of Pt ions is related to  $t_0 / \Delta_0$  by  $\rho \approx 1 - (t_0 / \Delta_0)^2$  well.<sup>1</sup> Consequently for the present substances one finds  $\rho \approx 0.93(0.92)$ , in good accord with previous x-ray photoemission spectroscopy<sup>47</sup> and x-ray absorption near edge structure<sup>41</sup> experiments. Furthermore, the quantity  $t_0 / \Delta_0$  is a key parameter for characterizing the self-localized excitations such as solitons and polarons. Viewed from a perturbation approach<sup>48</sup> the present result is reconciled with the experimental observations that the photoinduced neutral solitons are thermally mobile<sup>49,50</sup> despite that they are self-localized to have a very small size of subnanometer scale.<sup>51</sup>

The gap parameter  $\Delta_0$  is closely related to the properties of Pt-Cl bonds. Within the framework of the site-diagonal electron-lattice coupling scheme for the Peierls transition<sup>1-3</sup> the total energy of the ground state is minimized by balancing of the energy gain due to the electron-lattice coupling with the elastic energy needed to displace Cl ions. Provided the Pt-Cl bonds are harmonic, this condition is expressed by a relationship  $\beta\rho = Ku_0/2$ ,<sup>44</sup> which is equal to 2.5(2.3) eV/Å, between the coefficient  $\beta$  of the linear coupling of the valence electrons with the static displacement  $u_0 = 0.39(0.37)$  Å of Cl ions and the force constant  $K = 2M\omega_p^2 = 12.6(12.6)$  eV/Å<sup>2</sup> for the breathing mode, where  $M$  is the mass of a Cl ion. In the one-band model<sup>1-3</sup>  $\Delta_0$  is the energy that an electron of a Pt<sup>(3+ $\rho$ )+</sup> ion gains when two adjacent Cl ions go away by  $u_0$  toward Pt<sup>(3- $\rho$ )+</sup> ions, and thereby the harmonic approximation gives  $\Delta_0 = 2\beta u_0 = Ku_0^2/\rho = 2.1(1.9)$  eV.

These values of  $\Delta_0$  are significantly greater than  $\Delta_0 = 1.45(1.45)$  eV obtained from the present experiment. It

TABLE II. The zero-temperature self-energy  $\eta_0\Delta_0$ , transfer integral  $t_0$ , the ratio  $t_0/\Delta_0$ , the disproportionation  $\rho$  of Pt ions, and the empirical electron-lattice coupling constant  $\beta$  in the ClO<sub>4</sub> and BF<sub>4</sub> salts.

Substance	$\eta_0\Delta_0$ (eV)	$t_0$ (eV)	$t_0/\Delta_0$	$\rho$	$\beta$ (eV/Å)
ClO <sub>4</sub> salt	0.070	0.38	0.26	0.93	2.1
BF <sub>4</sub> salt	0.081	0.40	0.28	0.92	2.0

is noteworthy that in the harmonic approximation  $K$  is assumed to be independent of  $u_0$ . In general, however, the restoring force of a chemical bond depends on its valence state. In the present case, because of a large disproportionation of Pt ions, the Pt-Cl bonds must have a significant volume anharmonicity, that is,  $K$  must depend on  $u_0$  and bond lengths, although the equilibrium potential for a Cl ion in the vicinity of its minimum would be parabolic. This is evidenced by the fact that the breathing mode is softened by hydrostatic pressure.<sup>21,22,25,52-54</sup> The volume anharmonicity is manifested also by the fact that the force constant of the Pt<sup>(3+ $\rho$ )+</sup>-Cl bond is much greater than that of the Pt<sup>(3- $\rho$ )+</sup>-Cl bond.<sup>55</sup> If the dependence of  $K$  on the valence states of Pt-Cl bonds is treated empirically in terms of the Morse potential, the above-mentioned energy-minimum condition yields  $\beta\rho = 1.94$  eV/Å for the ClO<sub>4</sub> salt.<sup>21</sup> In the same way, for the BF<sub>4</sub> salt the Pt-Pt distance of 5.37 Å and the parameters  $u_0$  and  $K$  give  $\beta\rho = 1.87$  eV/Å. These empirical values of  $\beta\rho$  give  $\Delta_0 = 2\beta u_0 = 1.63(1.48)$  eV, in good agreement with the spectroscopic gap parameters obtained from the present experiment.

Actually, the Coulomb interactions would influence the interband optical transition. In the Hubbard model, letting the effective on-site and intersite Coulomb energies be  $U$  and  $V$ , respectively, the Coulomb interactions cause a shift of  $\hbar\omega_{\text{peak}}$  by  $3V - U$ .<sup>1-3</sup> In view of the results of the present study the value of  $|3V - U|$  is likely to be significantly smaller than 1 eV in both substances, although  $U$  and  $V$  could each be greater than or of the order of 1 eV.<sup>56</sup>

The values of basic quantities derived from the discussion in this section are summarized in Table II.

## V. CONCLUSIONS

The temperature dependence of the subgap optical absorption band associated with the fundamental Peierls gap in the low-temperature phase of the halogen-bridged linear-chain complexes [Pt(en)<sub>2</sub>][Pt(en)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> and [Pt(en)<sub>2</sub>][Pt(en)<sub>2</sub>Cl<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub> has been studied in the temperature range of 10–270 K. The results are found to be explained well in terms of the Kim-McKenzie-Wilkins theory which has formulated the smearing effect of the inverse-square-root singularity of the joint density of states due to the quantum and thermal lattice fluctuations. In particular, the observed thermal shift of the tail end of the absorption band has been successfully separated into the components arising from the Peierls gap and the fluctuation-induced subgap states.

It has been confirmed that the electron-phonon coupling is dominated by the breathing mode of Cl ions. Because of the one dimensionality of electronic bands and the high symme-

try of the breathing mode, the coupling is very strong. Consequently the thermal shift of the Peierls gap is induced by the self-energy effect due to the breathing mode: The self-energy of the renormalization of the Peierls gap amounts to 0.07–0.08 eV at 0 K. Correspondingly both substances have a large dimensionless electron-phonon coupling constant of  $\lambda \approx 1.2$ . The coupling of electrons with the  $2k_F$  mode is also so strong that a large Peierls gap of  $2\Delta_0 \approx 2.9$  eV opens in both salts. These findings give the transfer integral to be  $t_0 \approx 0.4$  eV and quantitatively explain the disproportionation

$\rho \approx 0.9$  of Pt ions. It is suggested that the volume anharmonicity of the Pt-Cl bonds plays an important role in the electron-lattice coupling.

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