

Optical properties of the cation-deficient platinum chain salt  $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$ 

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The room-temperature polarized reflectance of a potassium-deficient platinum chain salt  $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$  [K(def)CP] has been measured in the infrared and visible. The reflectance is strongly anisotropic, with a plasma edge in the red and high reflectance in the infrared for light polarized parallel to the Pt chain axis and almost frequency-independent reflectance for the transverse polarization. Analysis of the plasma edge indicates a nearly-free-electron mass for the conduction electrons. The data show the existence of an energy gap at room temperature and suggest a Peierls transition above room temperature. The parallel polarized reflectance has structure in the infrared which is the first direct evidence for strong coupling of the conduction electrons to the  $C \equiv N$  stretching vibration of the tetracyanoplatinate unit in quasi-one-dimensional platinum chain conductors.

## I. INTRODUCTION

Highly conducting linear chain inorganic complexes<sup>1,2</sup> have received considerable attention in recent years. Crystals of these materials typically consist of parallel linear chains of platinum (or other transition metal) atoms; this quasi-one-dimensional structure is often retained when chemical modifications are made. This property makes these platinum chain salts a particularly intriguing family in which it is possible to study the effects of chemical changes on the electronic properties of the compounds. We report here a study of the room-temperature optical properties of one of these systems,  $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$ , or K(def)CP.

The prototype platinum chain salt is  $K_2Pt(CN)Br_{0.30} \cdot 3H_2O$ , or KCP. In this compound the Pt  $d_{z^2}$  band is partially occupied leading to quasimetallic behavior for electronic motion along the Pt chain.<sup>1,2</sup> KCP and its chloro analog have a room-temperature conductivity of  $\sigma(295 \text{ K}) \approx 300 \text{ ohm}^{-1} \text{ cm}^{-1}$  and a Peierls metal-insulator transition occurring at 100 K.<sup>3</sup> Optical studies<sup>4-7</sup> have found plasma edge in the red with high reflectance below this edge. The optical studies also show that a Peierls transition occurs in KCP, as expected for a one-dimensional metal.<sup>7</sup> A weak gap is observed

at  $1600 \text{ cm}^{-1}$  (0.2 eV) at room temperature and evidence for a pinned Frölich mode is seen in the far infrared.<sup>5,7</sup>

K(def)CP differs from KCP in several important ways. Partial oxidation of the Pt chain in K(def)CP is obtained through synthesis of a potassium-deficient compound rather than through synthesis with excess bromide anions. The random potentials of the bromide anions, which are thought to be important for the electronic structure of KCP, are absent in K(def)CP. The stoichiometry indicates that the band filling (assuming a one-dimensional electron band) is  $\frac{7}{8}$  in K(def)CP while it is 0.85 in KCP. Structural studies by Keefer *et al.*<sup>8</sup> and Reis *et al.*<sup>9</sup> have shown that the Pt chains are not quite linear but instead form a zigzag pattern with a Pt—Pt repeat distance of four atoms, as shown in Fig. 1. The bond angles at every other site are  $173^\circ$  rather than the  $180^\circ$  of KCP. The Pt—Pt distance of 2.96 Å is slightly larger than in KCP (2.88 Å) while the tetracyanoplatinate moieties remain nearly perpendicular to the Pt chain direction. The tetramerization of the structure should split the single  $d_{z^2}$  band into four subbands with the highest one being half filled. A schematic one-electron band structure is shown in Fig. 2.

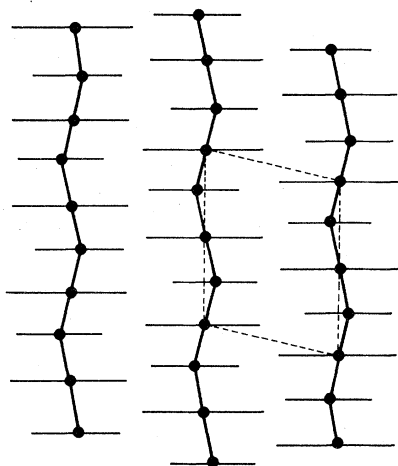


FIG. 1. Schematic illustration of the tetracyanoplatinate chains in K(def)CP projected onto (100). Cyan groups are displayed as horizontal lines of varying length depending on the staggering of each group. A single unit cell is enclosed by dotted lines. The distortion of the Pt chain is not to scale. (From Ref. 9.)

Because  $2k_F$  ( $k_F$  is the Fermi wave vector) in K(def)CP is commensurate with the lattice periodicity and because of the existing lattice distortion, the Peierls transition should occur at a higher temperature and the Peierls-distorted state should have a larger energy gap than in KCP. Inelastic neutron scattering studies by Carneiro *et al.*<sup>10</sup> have discovered a well-defined Kohn anomaly at 300 K while x-ray diffuse scattering studies by Schultz *et al.*<sup>11</sup> have revealed a superlattice line at  $2k_F$ . Diffuse x-ray measurements of Kobayashi *et al.*<sup>12</sup>

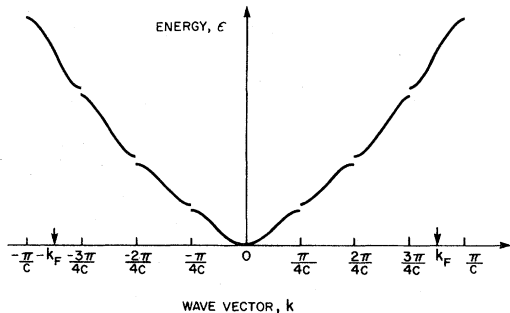


FIG. 2. Schematic illustration of one-electron band structure of K(def)CP. Here  $c$  is the Pt-Pt distance (one-fourth of the crystallographic repeat distance of four Pt atoms). The zigzag modulation of the Pt chain seen in Fig. 1 introduces band gaps at  $\pm\pi/4c$ ,  $\pm2\pi/4c$ , and  $\pm3\pi/4c$ . The Fermi wave vector is indicated at  $k_F = \pm\pi/8c$ . A gap is present at  $k_F$  below the Peierls-transition temperature.

have been interpreted as showing a  $2k_F$  to  $4k_F$  transition at 294 K.

dc electrical conductivity measurements in K(def)CP were reported by Epstein and Miller<sup>13</sup> and by Carneiro *et al.*<sup>14</sup> The temperature dependence of the conductivity, shown in Fig. 3, was unusual. Starting at the lowest temperatures, it first rose rapidly but then leveled off between 100 and 200 K. Above 200 K it again rose rapidly only to level off again above 300 K. Above 330 K the crystals suffered an irreversible water loss. Epstein and Miller<sup>13</sup> interpreted their data as showing a Peierls transition near 300 K with a strongly temperature-dependent energy gap below 300 K. Carneiro *et al.*<sup>14</sup> interpreted their data, which were essentially the same as that of Epstein and Miller, as showing a Peierls transition near 100 K with the temperature dependence at higher temperatures arising from the effects of water rotation.

The only previous optical studies of K(def)CP were reported by Musselman and Williams.<sup>15</sup> These measurements covered  $5000-25000\text{ cm}^{-1}$  (0.6–3.1 eV). For electric field parallel to the Pt chain a high “metallic” reflectance was observed in the infrared with a maximum value of 0.86 at  $8000\text{ cm}^{-1}$  (1 eV). A plasma edge was present at higher frequencies; the minimum reflectance occurred near  $22000\text{ cm}^{-1}$  (2.8 eV). The transverse reflectance was small ( $\sim 0.06$ ) and frequency independent.

In this paper we report the results of measure-

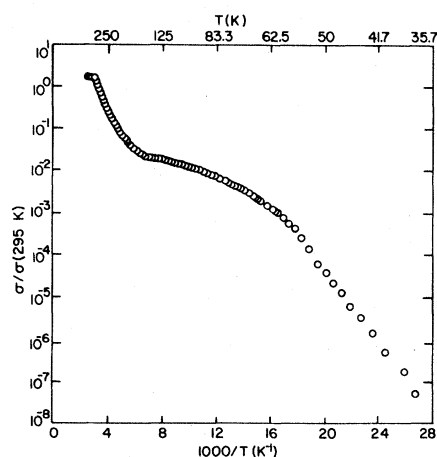


FIG. 3.  $\sigma(T)/\sigma(295\text{ K})$  on a logarithmic scale versus  $T^{-1}$  for a typical electrochemically grown crystal of K(def)CP. Note the four distinct regions,  $T > 310\text{ K}$ ,  $310 > T > 150\text{ K}$ ,  $150\text{ K} > T > 70\text{ K}$ , and  $T > 70\text{ K}$ . Measurements were made parallel to the Pt chain axis. (From Ref. 13.)

ments of the room-temperature polarized reflectance of K(def)CP in an expanded frequency regime, 800–26 000  $\text{cm}^{-1}$  (0.1–3.2 eV). These new results indicate that there is an energy gap in K(def)CP at room temperature and, for the first time, indicate that the conduction electrons are tightly coupled to the  $\text{C}\equiv\text{N}$  stretching mode of the tetracyanoplatinate unit.

## II. EXPERIMENTAL DETAILS

K(def)CP crystals were prepared by an electrochemical process which has been described previously.<sup>16</sup> Single crystals of approximately  $0.3 \times 3 \text{ mm}^2$  surface area were chosen for optical study. All crystals had some surface striations which made determination of the absolute reflectance values difficult. Attempts at polishing the crystals were not successful; polishing resulted in an infrared reflectance less than 0.1 in all cases. Viewed with electric field polarized parallel to the crystal long axis the samples had a metallic luster in the red, while under transverse polarization the reflectance was much lower and the samples were bluish in color.

Polarized reflectance measurements were made using a Perkin-Elmer grating monochromator with globar source and thermocouple detector over 800–4000  $\text{cm}^{-1}$ , and tungsten source and lead sulfide or photomultiplier detectors over 4000–26 000  $\text{cm}^{-1}$ . In addition, two samples were studied over 2000–8000  $\text{cm}^{-1}$  using the globar source and thermocouple detector to obtain a smooth connection between the data in the infrared and near-infrared regions. Polarizers used include wire grid, dichroic, and glass pile-of-plates. The reflectance apparatus used a large spherical mirror to focus the monochromator exit slit onto the crystal and second mirror to focus the reflected light onto the detector. In an earlier arrangement, the entire source output was focused on the sample and water loss due to the resultant heating was very evident. For some of the measurements, the sample was enclosed in a sealed water-containing cell. For other measurements the relative humidity exceeded 90% at the sample.

## III. EXPERIMENTAL RESULTS

Approximately 20 samples were investigated for this study. In no case did we measure an infrared reflectance exceeding 0.54; typical values were be-

tween 0.46 and 0.54 for energies near 8000  $\text{cm}^{-1}$  (1 eV). The results of our measurements are shown in Fig. 4, where we plot the polarized reflectance both parallel and perpendicular to the Pt chain over frequencies between 800 and 26 000  $\text{cm}^{-1}$  (0.1–3.2 eV). The chain-axis reflectance shows a strong feature between 1500 and 2000  $\text{cm}^{-1}$  (0.18 eV). At higher frequencies, the reflectance rises to a broad maximum at 8000  $\text{cm}^{-1}$  (1 eV) and then falls to a minimum at 21 800  $\text{cm}^{-1}$  (2.7 eV). The transverse reflectance is low, has structure at 2145  $\text{cm}^{-1}$  from the  $\text{C}\equiv\text{N}$  stretching mode, and shows little else of interest.

## IV. DATA ANALYSIS

### A. Fit to model dielectric function

We have fit the reflectance above 2000  $\text{cm}^{-1}$  to the customary Drude-Lorentz model. The complex dielectric function in this model is

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega/\tau}, \quad (1)$$

where  $\omega_p$  is the plasma frequency,  $\omega_0$  the resonant

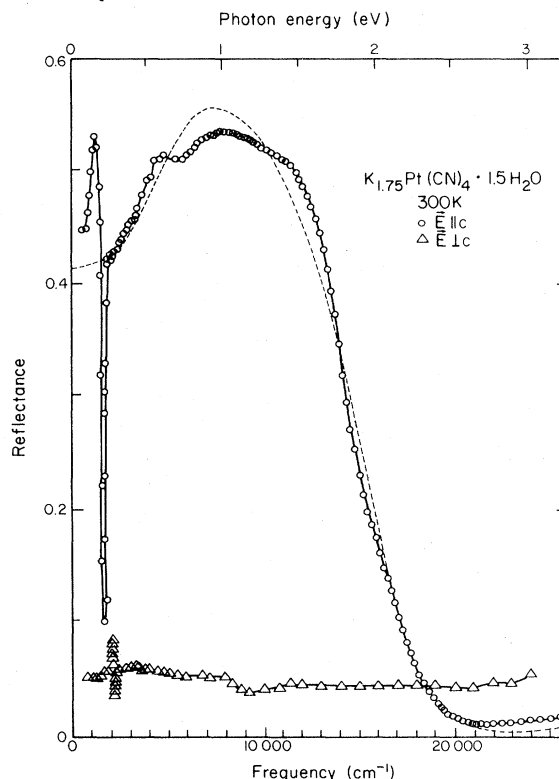


FIG. 4. Polarized reflectance of K(def)CP for electric field parallel and perpendicular to the platinum chain axis (c).

frequency of the single oscillator which the model assumes,  $\tau$  is the electronic lifetime, and  $\epsilon_\infty$  is the high-frequency dielectric constant. A least-squares fit to our chain axis data gives  $\omega_p = 23\,900\text{ cm}^{-1}$  (2.96 eV),  $\omega_0 = 5600\text{ cm}^{-1}$  (0.69 eV),  $1/\tau = 4800\text{ cm}^{-1}$  (0.60 eV) ( $\tau = 1.1 \times 10^{-15}$  sec), and  $\epsilon_\infty = 2.2$ . For comparison, the equivalent KCP values are<sup>4,7</sup>  $\omega_p = 2.93\text{ eV}$ ,  $\omega_0 = 0.16\text{ eV}$ ,  $\tau = 3.2 \times 10^{-15}$  sec, and  $\epsilon_\infty = 2.2$ ; only  $\omega_0$  differs significantly between the two compounds. The best fit to the reflectance is shown in Fig. 4 as a dashed line.

### B. Kramers-Kronig analysis

A Kramers-Kronig analysis of the reflectance to obtain the phase shift upon reflection is reasonably accurate because of the relatively wide frequency range employed (a factor of 30). Conventional extrapolation schemes were used to evaluate the Kramers-Kronig integral.<sup>7</sup> The reflectance was assumed to be constant at frequencies below the lowest measured point. It was extrapolated as  $1/\omega^2$  between 26 000 and 100 000  $\text{cm}^{-1}$  (simulating interband transitions) and as  $1/\omega^4$  at higher frequencies (as appropriate for free-electron behavior).

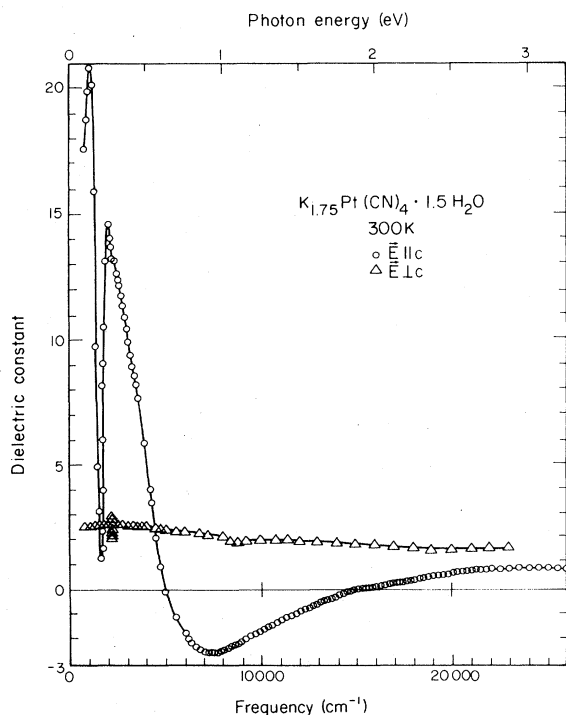


FIG. 5. Real part of the complex dielectric function of K(def)CP for two polarizations determined by Kramers-Kronig analysis of the reflectance.

Once the phase shift and reflectance are known, any of the optical constants may be calculated. We show in Fig. 5 the real part of the dielectric function  $\epsilon_1(\omega)$  for two polarizations. The low-frequency values suggest that the static dielectric constant of K(def)CP is 17 parallel to the Pt chain and 2.5 perpendicular to it.

Figure 6 presents the frequency-dependent conductivity  $\sigma_1(\omega)$  of K(def)CP obtained from the Kramers-Kronig analysis. At low frequencies, the infrared conductivity for electric field polarized parallel to the chain axis is 10–50  $\text{ohm}^{-1}\text{cm}^{-1}$ , close to the dc values reported previously.<sup>13,14</sup> There is a maximum at 1400  $\text{cm}^{-1}$  (0.17 eV) followed by a deep minimum at 1725  $\text{cm}^{-1}$  (0.21 eV). The conductivity then has a higher maximum, reaching a value of 1000  $\text{ohm}^{-1}\text{cm}^{-1}$  at 4500  $\text{cm}^{-1}$  (0.56 eV). Above this frequency the conductivity rolls off to a low value in the visible before rising again in the ultraviolet. The transverse polarization conductivity is nearly zero at low frequencies, shows a small peak at the C≡N stretching frequency, and rises steadily at higher frequencies.

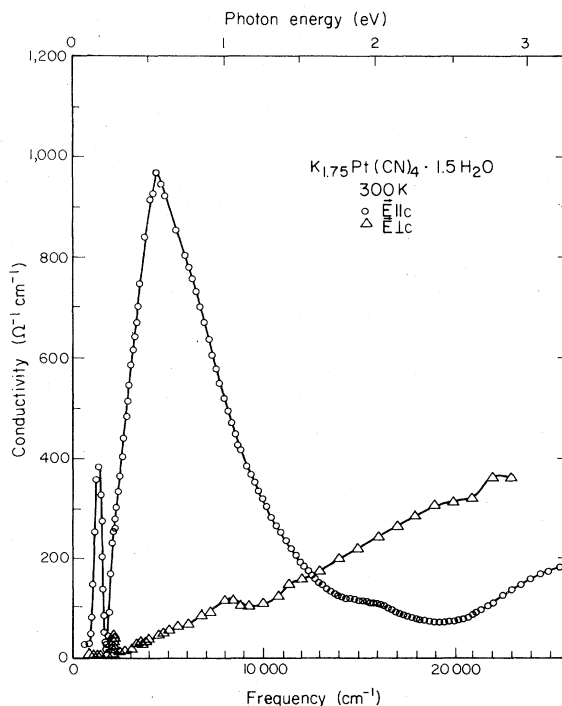


FIG. 6. Frequency-dependent conductivity of K(def)CP for two polarizations determined by Kramers-Kronig analysis of the reflectance.

## V. DISCUSSION

While our reflectance data are in good agreement with the measurements of Musselman and Williams<sup>15</sup> concerning the strong optical anisotropy, the location of the plasma minimum, and the qualitative shape of the reflectance at frequencies from the minimum to their lowest measured frequency of  $5000\text{ cm}^{-1}$ , the reflectance which they report is  $\sim 50\%$  larger than our measured values. Though the presence of some surface striations on the samples may have depressed the reflectance somewhat, it is unlikely that it would account for a factor of nearly 2. We do note, however, that the transverse reflectance that we obtained is close to that reported<sup>4</sup> for KCP.

### A. Electronic Structure

The plasma frequency obtained from the least-squares fit to the reflectance can be used to estimate the effective mass  $m^*$  of the conduction electrons, since  $\omega_p^2 = 4\pi n e^2 / m^*$ , where  $e$  is the electronic charge. The electron density  $n$  is evaluated assuming 1.75 valence electrons per platinum atom (obtained from the chemical formula), four Pt atoms per unit cell, and a crystallographic<sup>8,9</sup> unit cell volume of  $918\text{ \AA}^3$ . Using  $\omega_p = 23\,900\text{ cm}^{-1}$  and these parameters we obtain an effective mass near the free-electron value  $m$ :  $m^* = 1.2m$ . This result is slightly higher than the almost exactly free-electron value found for KCP.<sup>6</sup> Nevertheless, it is much smaller than the typical effective masses in organic one-dimensional crystals. The slight increase in effective mass above the free-electron value is probably an effect of the zigzag nature of the Pt chains, which introduce multiple energy gaps into the band structure at wave vectors  $k = \pi/(4c)$ ,  $\pi/(2c)$ , and  $3\pi/(4c)$  as shown schematically in Fig. 2.

Both the reflectance that we measure and the conductivity that we obtain from the Kramers-Kronig analysis have maxima near  $4500\text{ cm}^{-1}$  (0.55 eV) and fall at lower frequencies. KCP, in comparison, has only weak structure in the 300-K reflectance, which gives a broad conductivity maximum at  $1600\text{ cm}^{-1}$  (0.2 eV).<sup>7</sup> This maximum in KCP has been interpreted as reflecting a weak pseudogap at the Fermi level caused by the Peierls instability. We interpret our data in a similar fashion, except that in K(def)CP the gap appears to be a real gap because the conductivity shows a

sharp maximum with a low value at low frequencies.

As mentioned above there have been two different models proposed to account for dc electrical conductivity measurements in K(def)CP.<sup>13,14</sup> The presence of a real energy gap in our room-temperature data supports the conclusion<sup>13</sup> that the Peierls transition occurs at temperatures at or above room temperature. That is, the reflectance studies and the Kramer-Kronig analysis suggest that there is an energy gap at room temperature even though the dc conductivity is appreciable. The Drude-Lorentz dielectric function, Eq. (1), probably overestimates the energy gap, with  $\omega_0 = 0.69\text{ eV}$ . The frequency-dependent conductivity in Fig. 6 reaches one-half its maximum value of  $1000\text{ ohm}^{-1}\text{ cm}^{-1}$  at  $2800\text{ cm}^{-1}$  (0.35 eV) and one-quarter of its maximum value at  $1060\text{ cm}^{-1}$  (0.13 eV).

The exact criterion to be used to define the edge of a smeared gap is uncertain.<sup>18</sup> The dc-conductivity studies<sup>13</sup> suggested a temperature-dependent gap  $2\Delta$  of

$$2\Delta = 2\Delta_0(1 - T/T_c)^{1/2}. \quad (2)$$

The measured conductivity data for  $180 < T < 300\text{ K}$  were analyzed<sup>13</sup> yielding a zero-temperature gap of  $2\Delta_0 = 1700\text{ cm}^{-1}$  and a transition temperature of  $T_c = 308\text{ K}$ . At low temperatures the gap at  $k_F$  is expected to be well defined, with the energy versus wave-vector curve having zero slope at  $k_F$ . A well-defined gap would lead to band-edge singularities in the density of states. Within this picture, the low-temperature optical gap would be  $2\Delta_0 \approx 1700\text{ cm}^{-1}$ . As the temperature increases,  $2\Delta$  decreases according to Eq. (2). Evaluating Eq. (2) at 293 K results in a room-temperature gap of  $2\Delta = 375\text{ cm}^{-1}$  (0.05 eV). At this temperature, the gap width is comparable with thermal energy so the number of carriers excited into the conduction band will be large; the conductivity will also be significant. The exact details of the variation of the density of states at the band edge is uncertain at finite temperatures; however, above the transition the gap is reduced to zero and the energy versus  $k$  curve has finite slope around  $k_F$ . The frequency-dependent conductivity of Fig. 6 is in qualitative agreement with this picture, with an increasing conductivity for frequencies as low as  $800\text{ cm}^{-1}$  and with the conductivity approaching its maximum value for frequencies greater than  $2\Delta_0$ . This maximum is much larger than the measured dc conductivity indicating that the density of states retains some structure even at room temperature.

### B. Electron-intramolecular vibration interaction

A most intriguing feature of our data is the strong structure in the parallel polarized reflectance at frequencies between 1400 and 2000  $\text{cm}^{-1}$ . This feature results, we believe, from a coupling of the conduction electrons of the Pt chain to the  $\text{C}\equiv\text{N}$  stretching mode of the tetracyanoplatinate unit. It is the first infrared observation of an electron-intramolecular vibration interaction in an inorganic linear-chain compound.<sup>19</sup> This conduction-electron—molecular vibration interaction has been studied in several tetracyanoquinodimethane (TCNQ) compounds<sup>20–23</sup> and was suggested<sup>24</sup> to be important in the tetracyanoplatinate systems. This interaction has a profound effect on the optical properties for electric field polarized along the chain axis. In insulating compounds<sup>22,23</sup> the frequency-dependent conductivity exhibits a series of maxima at frequencies just below the totally symmetric (Ag) vibrational mode frequencies of the molecule. In contrast, small band-gap semiconducting systems<sup>20,21</sup> (those in which the electronic absorption overlaps the vibrational frequencies) show a series of indentations in the conductivity. Optical data have been analyzed in the past to obtain the strength of the electron-intramolecular vibration coupling in TCNQ salts.<sup>21,22</sup> We have carried out this analysis for K(def)CP.

Because the resonant frequency (or energy gap) inferred from the Drude-Lorentz fit is larger than the  $\text{C}\equiv\text{N}$  stretching frequency, we have tried to fit our data to the theory of electron-vibration coupling in dimeric systems.<sup>22</sup> [The structure of K(def)CP consists of tetramers; however, it has dimeric features in that the chain consists alternately of Pt atoms on the chain axis and Pt atoms displaced sideways from that axis; see Fig. 1.] A least-squares fit of the theory of Ref. 22 to our data, assuming a single mode, gave an electron-molecular vibration coupling constant of  $\lambda = 0.28 \pm 0.03$  and an unperturbed frequency of  $\omega_\alpha = 1600 \text{ cm}^{-1}$ . This frequency is far below the  $2100 \text{ cm}^{-1}$  expected for a  $\text{C}\equiv\text{N}$  stretching frequency. However, we were unable to obtain a fit if we forced the unperturbed frequency to be in the  $2100\text{-cm}^{-1}$  range. The observed frequency of the peak in the frequency-dependent conductivity is approximately<sup>22</sup>

$$\omega_{\text{obs}} \approx \omega_\alpha (1 - \lambda)^{1/2}.$$

With  $\omega_\alpha \approx 2100 \text{ cm}^{-1}$  and  $\omega_{\text{obs}} \approx 1400 \text{ cm}^{-1}$ ,  $\lambda \approx 0.56$ ; this very large value increases the calcu-

lated oscillator strength of the peak far above the observed strength.

An alternative analysis of the data can be made by assuming that the coupling gives rise to an indentation in the electronic envelope at  $1725 \text{ cm}^{-1}$ . In this case the “phase phonon” theory first applied<sup>21</sup> to  $\text{TEA}(\text{TCNQ})_2$  (TEA denotes triethylammonium) is used. Again, only one vibrational mode is important; this fact makes the analysis relatively straightforward. We start with Rice’s expression<sup>20,21</sup> for the static dielectric constant, written as a sum of polarizabilities,

$$\epsilon_0 = \epsilon_\infty + \frac{2\omega_p^2}{3(2\Delta_R)^2} + \frac{\Delta_R}{V} \frac{\omega_p^2}{(2\Delta_R)^2} \lambda, \quad (3)$$

where  $\epsilon_\infty$  includes the contribution of high-frequency electronic transitions to the dielectric constant, the second term results from transitions across the energy gap ( $2\Delta_R$  is the full gap) and the third term is an enhancement of the dielectric constant by the coupling to the vibrational modes. The parameter  $V$  that appears in Eq. (3) represents the strength of the  $2k_F$  component of the crystal potential which drives the lattice distortion. Each of the terms in Eq. (3) will contribute to the frequency-dependent dielectric constant at frequencies below its transition frequency and will not contribute at frequencies above the transition frequency. Thus

$$\epsilon(\omega) = \begin{cases} \epsilon_\infty, & \omega \gg 2\Delta_R \\ \epsilon_\infty + \frac{2\omega_p^2}{3(2\Delta_R)^2} \equiv \epsilon_{\text{el}}, & \omega_\alpha \ll \omega \ll 2\Delta_R \\ \epsilon_0, & \omega \ll \omega_\alpha \end{cases} \quad (4)$$

where  $\omega_\alpha$  is the frequency of the vibrational mode and  $\epsilon_{\text{el}}$  is the ordinary static dielectric constant of a one-dimensional semiconductor.<sup>25</sup>

The frequencies of the indentations in the conductivity are determined by the zeros of

$$D_\phi^{-1}(\omega) = \text{Re} \left[ D_0^{-1}(\omega) + 1 - \frac{V}{\Delta_R} \right] \quad (5)$$

with (assuming only a single vibrational mode)

$$D_0(\omega) = \frac{\omega_\alpha^2}{\omega_\alpha^2 - \omega^2 - i\omega\Gamma}, \quad (6)$$

where  $\Gamma$  is a phenomenological vibrational linewidth.

The frequency-dependent dielectric constant is plotted in Fig. 5. From this figure and our fit to the reflectance, we obtain  $\epsilon_\infty = 2.2$ ,  $\epsilon_{\text{el}} = 14$ , and  $\epsilon_0 = 18$ . These values in Eqs. (3) and (5) yield

$2\Delta_R = 4300 \text{ cm}^{-1}$  (0.53 eV) and  $\lambda\Delta_R/V = 0.21$ . Then, using  $\omega_\alpha = 2140 \text{ cm}^{-1}$  and setting  $D_\phi(\omega) = 0$  at  $\omega = 1725 \text{ cm}^{-1}$  (the observed frequency of the minimum in  $\sigma_1$ ), we obtain, for the dimensionless electron-phonon coupling constant,  $\lambda = 0.28$ . Interestingly, this value is the same as obtained from the fit to the theory for dimers.

This analysis yields a value for  $2\Delta_R$  larger than the frequency  $\omega_\alpha$  of the unperturbed vibrational mode. This result appears to be inconsistent with the assumption that the phonon frequency overlaps the electronic continuum. However, the "gap"  $2\Delta_R$  is in reality a parameter which characterizes the electronic structure of the semiconductor before the electron intramolecular vibration interaction is turned on. The conductivity can remain high at frequencies well below  $2\Delta_R$  because the gap is reduced by the interaction, because there is a finite density of states in the gap, and because lifetime effects smear the edge of the gap.

The large value of  $\lambda$  implies that the electron-intramolecular vibration interaction plays an important role in stabilizing the Peierls distortion in K(def)CP. The Peierls-transition temperature is determined by the strength of the electron-phonon interaction and by the width of the metallic band of the undistorted chain.<sup>26</sup> In K(def)CP the coupling constant is large, suggesting a strong-coupling equation should be used:

$$k_B T_p = E_F e^{-(1+\lambda)/\lambda} \quad (7)$$

The Fermi energy is of order  $E_F = \hbar^2 k_F^2 / 2m^* \sim 2.8 \text{ eV}$ ; our value of  $\lambda = 0.28$  then yields  $T_p = 330 \text{ K}$ . This value is a lower limit; coupling to phonons at frequencies below our experimental range [for example, in both KCP (Ref. 27) and K(def)CP (Ref. 10) acoustic phonons are important for the Peierls transition] will increase  $\lambda$  and the estimate of  $T_p$ . A transition temperature of 330 K is, however, in good agreement with the results of the dc-conductivity study of Epstein and Miller.<sup>13</sup>

The strong coupling of electrons to the high-frequency intramolecular vibration may have profound effects on the dc conductivity of platinum chain compounds. A calculation<sup>28</sup> of the temperature dependence of the mobility of the electrons thermally activated into the conduction band and scattering from optical phonons gives a mobility approximately proportional to  $T^{-5}$ . This mobility combined with the temperature dependence of the carrier density reproduces the dc conductivity of such platinum chain salts as KCP and  $\text{Cs}_{1.75}\text{Pt}(\text{CN})_4 \cdot 1\text{H}_2\text{O}$ .

## VI. SUMMARY

K(def)CP has a larger gap and higher Peierls-transition temperature than KCP. Three factors probably contribute to the difference between the two compounds. The Fermi wave vector in K(def)CP is commensurate with the crystal lattice; the commensurability helps stabilize the distorted state. Second, the chains are distorted; their zigzag structure leads to a tetrameric repeat along the chain which does not by itself induce a gap at the Fermi surface but which does provide an additional periodic potential for the electrons. This potential introduces gaps in the band structure and raises the commensurability from that of a seven-eighths-filled band to that of a one-half-filled band; half-filled one-dimensional systems almost invariably suffer Peierls transitions at relatively high temperatures. Finally, the crystallographic inequivalence of the Pt sites, the (small) alternation in Pt-Pt separation, and the (small) nonplanarity of the  $\text{Pt}(\text{CN})_4$  may allow a larger coupling between the conduction-electron  $d_{z^2}$  orbitals and the molecular vibrations. Without these deviations, the overlap between the even  $d_{z^2}$  orbitals and the odd  $\text{C}\equiv\text{N}$  vibrational mode would vanish in first order. Hence a larger electron-molecular vibration coupling is expected in K(def)CP as compared to KCP.

We have reported here the room-temperature infrared and visible properties of K(def)CP. The reflectance was strongly anisotropic, with a plasma edge in the red. There was high reflectance in the infrared for light polarized parallel to the platinum chain axis and almost frequency-independent reflectance for the transverse polarization. For the parallel direction a least-squares fit gave a plasma frequency of  $23\,900 \text{ cm}^{-1}$  together with an effective mass of  $1.2m$ . The parallel polarized reflectance revealed the first direct evidence for strong coupling of the conduction electrons to an intramolecular vibration in an inorganic (e.g., Pt chain) quasi-one-dimensional conductor. An analysis of this effect was made in terms of Rice's<sup>20,21</sup> phase phonon theory.

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