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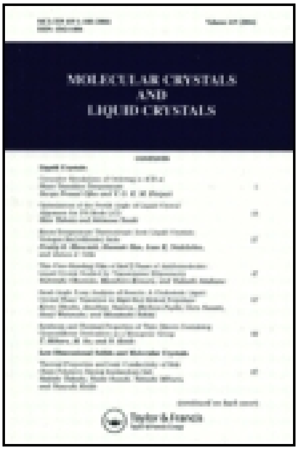

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Evidence for Conduction Electron-Intramolecular Vibration Interaction in a Platinum Chain Salt

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EVIDENCE FOR CONDUCTION ELECTRON-INTRAMOLECULAR VIBRATION INTERACTION IN A PLATINUM CHAIN SALT

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Polarized reflectance measurements on $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$, or K(def)CP reveal that there is a deep indentation in the chain-axis reflectance at a substantially lower frequency (1725 cm^{-1}) than the ordinary $C \equiv N$ stretching frequency (2180 cm^{-1}). The frequency-dependent conductivity, found by Kramers-Kronig analysis of the reflectance, has a deep antiresonance at about the same frequency. This structure is attributed to a phase-phonon mode of the coupled electron-intramolecular vibration system. These data provide the first direct evidence for the importance of the interaction of the conduction electrons with molecular vibrations in a metal chain compound. The dimensionless electron phonon coupling constant is estimated to be $\lambda \sim 0.28$, a result which suggests that this interaction might be important for stabilizing the Peierls distortion in K(def)CP and that it might influence the dc conductivity of the material.

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INTRODUCTION

In this paper, we present evidence for strong coupling of the conduction electrons to intramolecular vibrations in a platinum chain salt. This evidence comes from polarized reflectance measurements on $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$, or K(def)CP. The conduction electrons on the Pt chain interact strongly with the symmetric stretching vibration of the C ≡ N groups in the tetracyanoplatinate unit.

Although electron-molecular vibration interactions are well known to be important for the properties of organic linear chain systems (such as salts of tetracanoquinodimethane or TCNQ) and have been extensively studied both theoretically[1-3] and experimentally,[4-6] these effects have not previously been observed in a platinum chain system.[7] When the vibrational frequency occurs in an electronic continuum (as we believe to be the case for K(def)CP), the effect is manifested as a dip or antiresonance in the chain-axis polarized reflectance and conductivity.[1,2] The frequency at which the minimum occurs is typically lower than that of the bare vibrational mode; the amount of red shift is determined by the strength of the electron-vibration coupling and by the polarizability of the electronic background.

In K(def)CP, partial oxidation of the Pt chain results from the potassium deficiency.[8] The structure is ordered; there is a slight zig-zag to the Pt chain with a repeat distance of four Pt atoms.[9,10] This tetramerization splits what would be a 7/8-filled electron energy band into four subbands with the highest one being half-filled.

Electrical transport and optical studies of K(def)CP have been previously reported.[11-13] The room-temperature electronic structure of the material has been recently discussed by Greene et al.[14] The conduction electrons were found to have a nearly free-electron effective mass , $m^* \sim 1.2\ m_e$. There is evidence for a gap in the absorption spectrum at $E_g \simeq 0.5$ eV while temperature-dependent dc conductivity studies[11] yield a somewhat lower gap estimate at low temperatures, $E_g = 2\Delta_0 \sim 0.21$ eV. Luminescence measurements by Stegmeier et al.[15] indicate a lower gap value and show clear evidence for a $2k_F$ interaction between the charge density wave (CDW) and the C ≡ N stretching mode.

II. EXPERIMENTAL DETAILS AND RESULTS

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The room-temperature polarized reflectance of electrochemically grown[16] K(def)CP single crystals, having ∼ 0.3x3mm^2 surface area, was measured over the frequency range 800-26000 cm^{-1} (0.1-3.2 eV) by using a reflectance spectrometer built around a Perkin-Elmer model 16V monochrometer.[6] The reflectance for frequencies between 1000 and 3000 cm^{-1} is shown in Figure 1. For electric field along c (the chain axis) the reflectance over most of the region is $R_{||} \sim 0.4$. There is a deep minimum ($R_{||} \sim 0.1$) at $\omega \sim 1670$ cm^{-1}. The transverse reflectance is low ($R_{\perp} \sim 0.06$). The ordinary C ≡ N stretching mode is seen in $R_{\perp}$ as the structure at 2145 cm^{-1}.

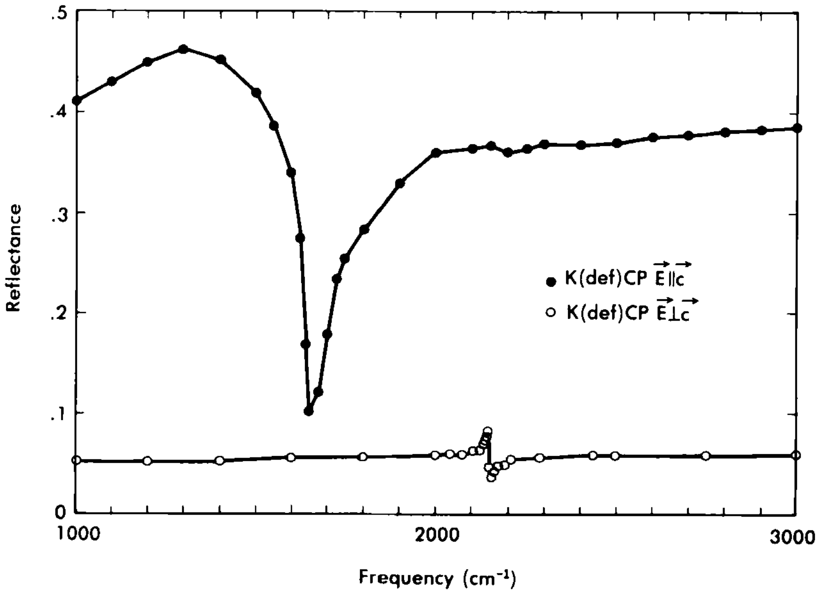

FIGURE 1. Polarized reflectance of K(def)CP for electric field parallel and perpendicular to the platinum chain axis (c).

The reflectance data were analyzed by Kramers-Kronig techniques to obtain the optical constants.[17] The frequency-dependent conductivity, $\sigma(\omega)$, for $1000 \leq \omega \leq 3000$ cm^{-1} is shown in Figure 2. As in the case of the reflectance, there is a deep minimum in $\sigma(\omega)$ for E parallel to c, at 1725 cm^{-1}. Note that at ω = 1000 cm^{-1}, σ (ω) = 100 Ω^{-1}cm^{-1}, in

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excess of the 300K dc value[11] $\sigma_0 \approx 40\ \Omega^{-1}\mathrm{cm}^{-1}$. For E perpendicular to c, the conductivity is small and rises slowly with increasing frequency and shows the C ≡ N stretch at 2145 cm^{-1}.

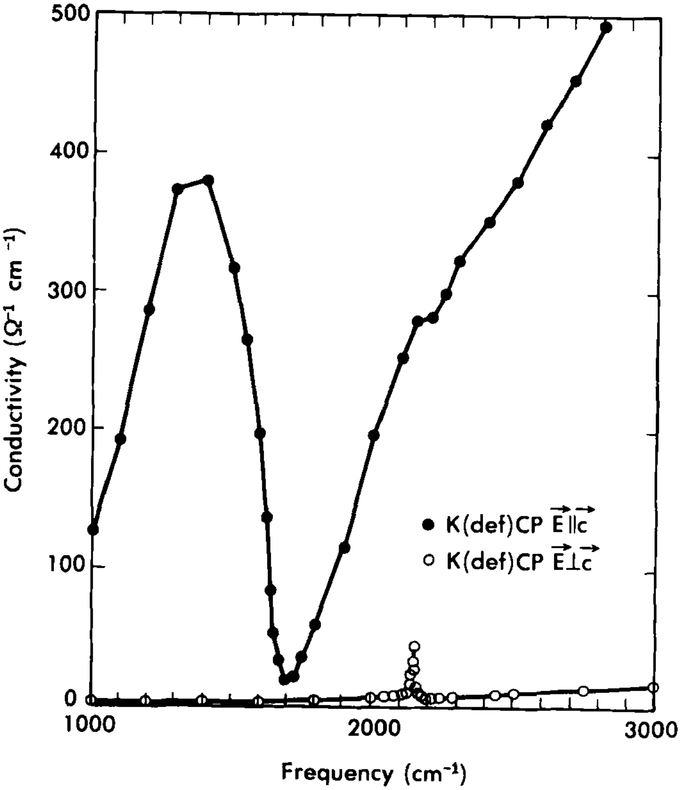

FIGURE 2. The frequency-dependent conductivity of K(def)CP for two polarizations determined by Kramers-Kronig analysis of the reflectance.

III. DISCUSSION

The phase-phonon mechanism[1,2] for infrared activity of ordinarily inactive vibrational modes induces very intense structure to appear in the chain-axis reflectance or conductivity of a one-dimensional Peierls insulator. When the frequency of the ordinary vibrational mode occurs in an electronic

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continuum, the structure is a dip or antiresonance at a somewhat lower frequency than the bare vibrational frequency. The feature is electronic in origin because it arises from an oscillation of the phase of the charge density wave in the Peierls-distorted one-dimensional material about its equilibrium value. This phenomenon is similar to the Fano antiresonance[18] observed in atomic systems when a narrow energy level interacts with a continuum.

A complete theory for the phase-phonon effect and for its influence on the Peierls transition has been given by Rice.[1,2] He showed that the frequencies of the antiresonances in the conductivity are determined by

$$\mathrm{Re}\left\{ D_o^{-1}(\omega) + 1 - V/\Delta_R \right\} = 0 \qquad (1)$$

In this equation, V represents the strength of the $2k_F$ component of a periodic potential which induces the Peierls distortion (it is also the half-energy gap in the absence of the Peierls distortion) and Δ_R is the half-gap of the stabilized Peierls insulator. The remaining term is an oscillator function

$$D_o(\omega) = -\sum_\alpha \frac{(\lambda_\alpha/\lambda)\,\omega_\alpha^2}{\omega_\alpha^2 - \omega^2 - i\omega\Gamma_\alpha} \qquad (2)$$

where the index α runs over all the symmetry-allowed modes, Γ_α is a phenomenological linewidth (here assumed to be small), ω_α is the frequency of the unperturbed vibrational mode, λ_α is the dimensionless-electron-phonon coupling constant of the α th mode, and $\lambda = \sum_\alpha \lambda_\alpha$ is the total electron-phonon coupling constant. In our data, we see only a single feature, which we assign to a phase-phonon arising from the C ≡ N stretching vibration. Because there is only one mode, we assume $\lambda_\alpha = \lambda$ and we take $\omega_\alpha = 2140\mathrm{cm}^{-1}$. Before the coupling constant can be obtained, we need values for the remaining parameters in equation (1), V and Δ_R. The phase phonon enhances the static dielectric constant, ε_o, above what it would be if there were no coupling. According to Rice, Pietronero and Bruesch[2]

$$\varepsilon_o = \varepsilon_\infty + \frac{2}{3}\,\frac{\omega_P^2}{(2\Delta_R)^2} + \frac{\Delta_R\,\omega_P^2}{V\,(2\Delta_R)^2} \qquad (3)$$

where the first term is the high frequency dielectric constant, the second arises from transition across the Peierls gap, and the third comes from the phase-phonons. Each of these terms contributes to the dielectric constant at low frequencies and then drops out when the frequency exceeds the transition frequency. Thus

$$\varepsilon(\omega) \simeq \begin{cases} \varepsilon_{\infty} + \frac{2}{3}\,\frac{\omega_p^2}{(2\Delta_R)^2} \equiv \varepsilon_{el} & \omega_\alpha \ll \omega \ll 2\Delta_R \\ \varepsilon_0 & \omega \ll \omega_\alpha \end{cases} \qquad (4)$$

From our Kramers-Kronig results,[14]

$$\begin{aligned} \varepsilon_{el} &= 14 \\ \varepsilon_0 &= 18 \end{aligned} \qquad (5)$$

These values in equations (3) and (4) give $2\Delta_R = 4300\ \mathrm{cm}^{-1}$ and $\lambda(\Delta_R/V) = 0.21$. Then, evaluating equation (1) at $\omega = 1725\ \mathrm{cm}^{-1}$, where the antiresonance occurs, we obtain $\lambda = 0.28$.

The value for λ is relatively large, implying that the interaction of the conduction electrons with this intramolecular vibration plays an important role in stabilizing the Peierls transition. The large value also suggests that a strong-coupling equation should be used to estimate the transition temperature:

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

with $E_F = \hbar^2 k_F^2/2m^* = 2.8$ eV, we obtain $T_p \simeq 330$K. This temperature is in good agreement with the results of dc-conductivity studies of Epstein and Miller.[11]

Strong electron-molecular vibration coupling is not observed[19] in $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$ (KCP). The difference between K(def)CP and KCP probably arises from the differences[9,10] in structure. In K(def)CP the Pt chains have a zig-zag pattern while they are linear in KCP. For linear chains, the

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coupling between the d_{z^2} orbitals of the electrons and the C ≡ N vibrational mode vanishes in first order. The broken symmetry of the Pt chains in K(def)CP permits the coupling to occur.

IV. SUMMARY

In summary, we have found the first direct evidence for the coupling of intramolecular vibrations to the conduction electrons in an inorganic Pt chain salt. This coupling has important consequences for the Peierls transition in K(def)CP as well as for the optical and transport properties.

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