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Gap states of polaron and associated optical absorption in the quasi-one-dimensional solid $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$

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Abstract. The energy spectrum and the optical absorption coefficient $\alpha(\omega)$ of a hole polaron in a PtCl chain are numerically calculated on the basis of the Baeriswyl–Bishop model. In intermediate coupling, there appear some shallow gap states as well as deep gap states, both of which give contributions to the absorption. The three-band structure of the absorption in the near- and mid-infrared region is consistent with the experimental data on $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$. The theory also shows that in the far-infrared region there is another absorption near 500 cm^{-1}, which is associated with the shallow gap states.

1. Introduction

Optical properties of the quasi-one-dimensional solid $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ ('en' is short for ethylenediamine) have been of considerable interest in recent years, particularly as they provide a typical example for the one-dimensional charge-density-wave (CDW) state [1–7]. This material is composed of transition-metal ions Pt^{3+} bridged by halogen ions Cl^-. A Pt ion has an unpaired electron in its d_z orbital ($\hat{z}$ is parallel to the chain), and this orbital makes an energy band through the supertransfer between two neighbouring d_z orbitals. This supertransfer comes from the hybridization between the d_z orbital and the p_z orbital of Cl ions. Thus, this system is expected to be a metal with a half-filled energy band.

Because of the electron–phonon coupling, however, charge transfer occurs between two neighbouring Pt ions so as to give the following mixed-valence state

$$-Cl^- -Pt^{(3+\delta)+} -Cl^- - Pt^{(3-\delta)+} -Cl^- -Pt^{(3+\delta)+} -Cl^- -$$
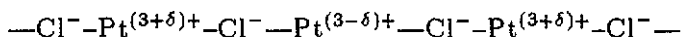
($0 < \delta < 1$) wherein Cl^- has displaced towards $Pt^{(3+\delta)+}$ (where δ denotes the degree of charge transfer). This is just the CDW with a commensuration of 2. This state has a strong optical absorption band in the visible region, and it is called the charge-transfer (CT) excitation band. When this CT band is excited by intense

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light, two new absorption bands appear, as shown by Kurita *et al* [3, 4]. These photoinduced absorption bands are named A and B, and their energies are about 1.68 and 2.0 eV respectively. Very recently another photoinduced absorption band was found in the mid-infrared region [5]. It is named C and its energy is about 0.3 eV. In view of the similarity of the theoretical description [8, 9, 14] of this material to the Su–Schrieffer–Heeger (SSH) model [10] or the Takayama–Lin-Liu–Maki (TLM) model [11] of polyacetylene, these absorption bands are considered to be associated with the defects—solitons, polarons or bipolarons. Gammel *et al* further developed a two-band model [20] for the M–X system. Nasu and co-workers investigated the lattice relaxation paths of photogenerated CT excitation [21]. But there are some controversies about the interpretation of the absorption. For instance, Kuroda and Sakai *et al* [1, 2] have interpreted the A and B bands in terms of the soliton model. On the other hand, Kurita *et al* [3] and Donohoe *et al* [5] have attributed the bands to the polaron absorptions. By proposing a mixed-valence linear chain model, Baeriswyl and Bishop (BB) have described the exciton, the polaron and the solitonic defects of the chain in the strong limit of electron–phonon coupling [14]. Onodera has studied the situation in the weak limit [9]. Most explanations for the absorption bands are based on the above theoretical descriptions.

It should be mentioned that the electron–lattice coupling in real materials is intermediate. And, in such a case, besides the well known gap states of the defects, which have been called the deep gap states in polyacetylene [22, 23], there will appear some shallow bound electronic states trapped by the defects. Such shallow gap states have been found in the case of the soliton in M–X compounds [15, 16]. These shallow gap states, as well as the deep gap states, can give a contribution to the optical absorption. In this paper we are going to find all the gap states of the polaron in the M–X compound and calculate the absorption coefficient $\alpha(\omega)$ associated with both shallow and deep gap states, and then try to understand the observed bands in the experiments.

2. Polaron state

We start from the CDW limit of the BB model [14]. The Hamiltonian is

$$
\begin{aligned}
H = &-\sum_{n,\sigma} \beta(v_{n+1} - v_n) C_{n,\sigma}^{\dagger} C_{n,\sigma} - \sum_{n,\sigma} t_0 (C_{n,\sigma}^{\dagger} C_{n+1,\sigma} \\
&+ C_{n+1,\sigma}^{\dagger} C_{n,\sigma}) + \tfrac{1}{2} K \sum_{n} (v_n^2 + v_{n+1}^2)
\end{aligned}
\tag{2.1}
$$

where the operators $C_{n,\sigma}^{\dagger}$ create (and the operators $C_{n,\sigma}$ annihilate) an electron at the nth Pt ion with spin σ, v_n are the displacement coordinates of Cl ions, β is the electron–phonon coupling strength and K is the force constant. In equation (2.1), t_0 is the supertransfer between two neighbouring Pt ions. In general it will be a function of the distance between two Pt ions at sites n and $n + 1$. In the case of a CDW state, Pt ions remain motionless, so t_0 is a constant. Introducing the dimensionless parameters ϕ_n and λ,

$$
\phi_n = (-1)^n (\beta/t_0) v_n \qquad \lambda = \beta^2 / \pi K t_0
\tag{2.2}
$$

we have

$$H/t_0 = -\sum_{n,\sigma}(-1)^n(\phi_{n+1} + \phi_n)C_{n,\sigma}^\dagger C_{n,\sigma} - \sum_{n,\sigma}(C_{n,\sigma}^\dagger C_{n+1,\sigma}$$

$$+ C_{n+1,\sigma}^\dagger C_{n,\sigma}) + \frac{1}{\lambda\pi}\sum_n \phi_n^2. \tag{2.3}$$

Equation (2.3) shows that if we measure energy in units t_0, the properties of the chain system depend only on the electron–phonon coupling λ. The electron spectrum ϵ_μ^σ and the corresponding wavefunction $\psi_\mu^\sigma(n)$ are determined by the eigenequation of the Hamiltonian (2.3),

$$\epsilon_\mu^\sigma\psi_\mu^\sigma(n) = (-1)^n(\phi_{n+1} + \phi_n)\psi_\mu^\sigma(n) - [\psi_\mu^\sigma(n) + \psi_\mu^\sigma(n-1)]. \tag{2.4}$$

Supposing a small deviation $\{\delta\phi_n\}$ from the lattice configuration $\{\phi_n\}$, the total energy of the chain system can be written as

$$E(\{\delta\phi_n\}) = E_0 + E_p + \sum_n A_n\delta\phi_n \tag{2.5}$$

where E_0 is the ground-state energy and E_p the polaron energy, and

$$A_n = (-1)^n \sum_{\mu(\text{occ.}),\,\sigma} [\psi_\mu^\sigma(n)\psi_\mu^\sigma(n) - \psi_\mu^\sigma(n-1)\psi_\mu^\sigma(n-1)] + \frac{2\phi_n}{\lambda\pi}. \tag{2.6}$$

As the coefficients A_n approach zero, the total energy reaches its minimum value. Then the configuration ϕ_n will be the self-consistent static configuration,

$$\phi_n = \tfrac{1}{2}\lambda\pi(-1)^n \sum_{\mu(\text{occ.}),\,\sigma} [\psi_\mu^\sigma(n-1)\psi_\mu^\sigma(n-1) - \psi_\mu^\sigma(n)\psi_\mu^\sigma(n)]. \tag{2.7}$$

Solving these combined equations (2.4)–(2.7), the electronic spectrum and the lattice relaxation can be obtained. In order to yield a positively charged polaron, we take a ring with 80 PtCl monomers and 79 electrons to perform the numerical iterations. Our accuracy is better than 10^{-5}. The electron–phonon coupling strength is assumed to be $\lambda = 0.41$ in view of the far-infrared optical measure for the material $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ [17]. According to [2] and [15], the supertransfer $t_0 = 0.5$–0.7 eV. We set $t_0 = 0.52$ eV in the present calculation [2].

We present our results in figures 1–3. The static polaron configuration $\{\phi_n\}$ is shown in figure 1(a) and the charge-density profile $\langle C_n^\dagger C_n \rangle$ in figure 1(b). From these results we can see that the polaron distortion involves about 10 monomers. Far from the polaron the order parameter $\bar{\phi}_n \simeq 1.11$ and the charge deviation $\delta \simeq 0.86$. The data are consistent with the experimental observation of the material $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ in the ground state. The electron spectrum is shown in figure 2. The width of the Peierls gap is about 2.67 eV. There are four levels in the gap. The corresponding wavefunctions are illustrated in figure 3. Among them ϵ_{vd} and ϵ_{cd} are deep levels which correspond to the intra-gap localized polaron states in the TLM model, and the levels ϵ_{vs} and ϵ_{cs} are shallow levels near the conduction band (CB) and the valence band (VB). In the previous theories, in both the strong and the weak electron–phonon coupling limits, only two localized electron states, the deep gap states, are considered; another two localized states, the shallow gap states, are missed.
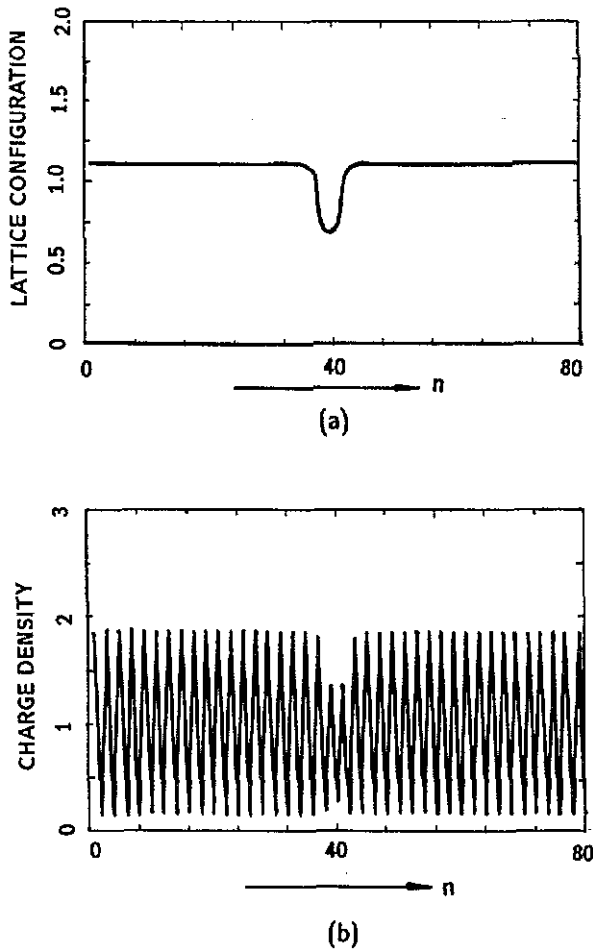
Figure 1. (a) The lattice relaxation ϕ_n and (b) charge-density profile $\langle C_n^\dagger C_n \rangle$ of a PtCl chain containing a hole polaron.

3. Optical absorption

The clearest signature of the non-linear excitations in the material [Pt(en)$_2$][Pt(en)$_2$ Cl$_2$](ClO$_4$)$_4$ is its intra-gap optical absorptions. In this section, we calculate the optical absorption coefficient associated with a hole polaron. We use the optical absorption formalism for discrete systems developed by Phillpot *et al* [18]. Within the framework of linear response, the optical absorption coefficient $\alpha(\omega)$ is expressed as

$$\alpha(\omega) \equiv \operatorname{Re} \sigma(\omega) = \frac{1}{\omega N} \sum_{\mu\nu} \sum_n |\langle \psi_\mu(n)|J(n)|\psi_\nu(n)\rangle|^2 \delta(\epsilon_\mu - \epsilon_\nu - \omega) \qquad (3.1)$$

where $\sigma(\omega)$ is the conductivity, J the current-density operator and N the number of monomers, $\psi_\mu(n)$ is the value of the wavefunction at the nth site and for an electron in the μth level. The level μ is empty and the level ν is occupied. Defining the charge density as $\rho_n = e C_n^\dagger C_n$ and relating it to the current density through the
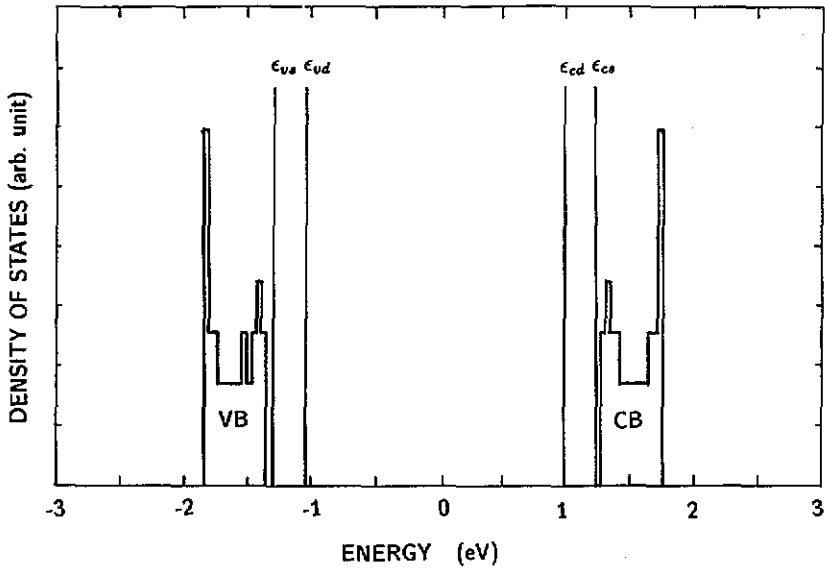
Figure 2. Electronic spectrum of a hole polaron.

equation for charge conservation, one finds [19]

$$J(n) = iet_0(C_{n+1}^\dagger C_n - C_n^\dagger C_{n+1}). \qquad (3.2)$$

Using equation (3.2), equation (3.1) may be expressed as

$$\alpha(\omega) = \pi e^2 t_0^2 \left(\frac{1}{\omega N}\right) \sum_{\mu,\nu} |M_{\mu,\nu}|^2 \delta(\epsilon_\mu - \epsilon_\nu - \omega) \qquad (3.3)$$

with

$$M_{\mu,\nu} = \sum_n \left[f_\mu(n) f_\nu^*(n+1) - f_\nu(n) f_\mu^*(n+1) \right] \qquad (3.4)$$

where $f_\mu(n)$ is the amplitude of the wavefunction of the μth level at the nth site. In addition, consideration of the oscillator strength leads to the sum rule

$$\int_0^\infty \alpha(\omega)\, d\omega = -\left(\frac{\pi e^2}{2N}\right) \langle H_J \rangle \qquad (3.5)$$

where $\langle H_J \rangle$ is the expectation value of the part of the Hamiltonian that contributes to the current operator. Correct implementation of equations (3.3) and (3.4) can be verified by the satisfaction of this sum rule.

Figure 4(a) shows our numerical result for the optical absorption associated with the hole polaron. In the calculation, the δ function in (3.3) has been substituted by a Lorentz profile with width 0.2 eV. Our numerical calculation obeys the sum rule better than 95%. Figure 4(b) shows the optical absorption of a perfectly 'dimerized' chain. Figure 4(c) is the difference between the optical absorptions of the chain containing a hole polaron and the same chain in its ground state.
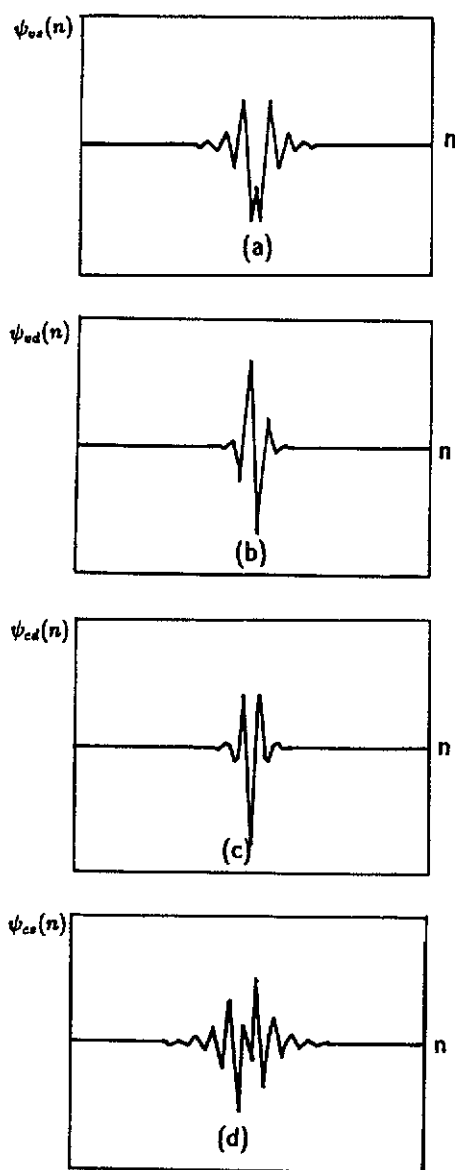
Figure 3. The wavefunctions of the four bound states trapped by a hole polaron.
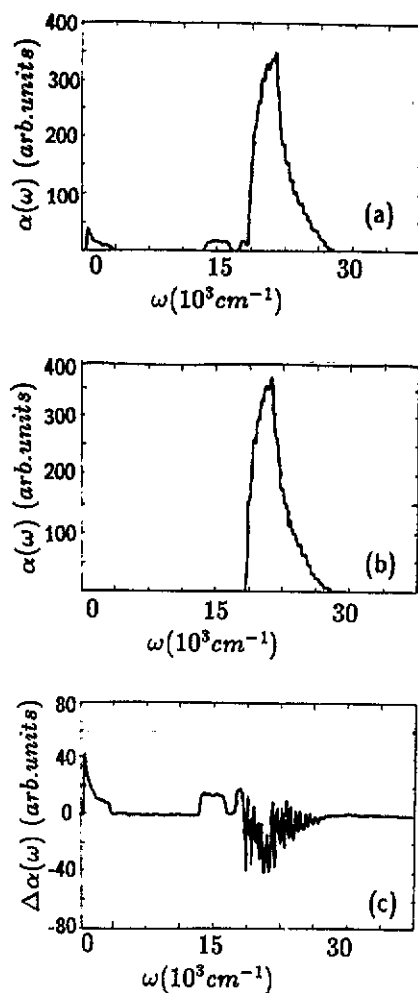

Figure 4. Optical absorption coefficient $\alpha(\omega)$ of a PtCl chain: (*a*) containing a hole polaron; (*b*) in its ground state; (*c*) difference $\Delta\alpha(\omega)$ between the optical absorption of a PtCl chain containing a hole polaron and the same chain in its ground state.

From these results it can be seen that there are two bands in the near-infrared region (2.1 and 1.8 eV) and one band in the mid-infrared region (0.3 eV). They are consistent with the three-band structure of the optical absorption observed in $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$. In the right-hand side of the figure 4(*c*), the bleaching

effect in the CT band has been apparently demonstrated. Interestingly, figure 4(c) also shows a cusp in the left-hand side of the third band; the energy of this cusp (0.06 eV) is about equal to the separation between the shallow gap states and the band edges. It implies that in the far-infrared region there can exist one more absorption band near 500 cm^{-1}, which is associated with the shallow gap states.

4. Conclusion and discussion

In conclusion, we have performed a numerical simulation of electronic states and optical absorption of a positively charged polaron in the quasi-one-dimensional material [Pt(en)$_2$][Pt(en)$_2$Cl$_2$](ClO$_4$)$_4$ on the basis of the Baeriswyl–Bishop model. Two new levels are found in the Peierls gap. They are shallow levels near the edges of CB and VB, distinct from the intra-gap levels in the strong or weak limit. The width of the gap, the displacement of Cl ions and the charge deviation agree with the experimental data. The three-band structure of optical absorption is basically consistent with the experimental observation.

The results of the present work support the hole polaron model of optical absorption. The authors of the present paper have worked out the optical absorption associated with the charged and neutral solitons by using the electronic states of [15] and [16]. Soliton absorption is qualitatively not consistent with the experimental data. On the other hand, experimentally one expects that holes are the predominant species [13]. Therefore, we interpret the three observed absorption bands as follows: A, $\epsilon_{vd} \rightarrow \epsilon_{cd}$; B, $\epsilon_{vd} \rightarrow \epsilon_{cs}$; C, $\epsilon_{vs} \rightarrow \epsilon_{vd}$. The explanation confirms the analysis given by Donohoe *et al* [5] recently. In addition, our theoretical result shows that there is a cusp near 500 cm^{-1} in $\alpha(\omega)$, which is associated with the shallow gap states. It predicts that in the far-infrared region there is another absorption band.

There is some deviation in detail between the present theory and the experimental data. It probably originates from two main reasons: the Coulomb interaction and the p_z orbit of the Cl ion, which are neglected. Further calculations should take the two factors into account.

References

[1] Kurita N, Sakai M, Nishina Y, Tanaka M and Kurita S 1987 *Phys. Rev. Lett.* **58** 2122
[2] Sakai M, Kuroda N and Nishina Y 1989 *Phys. Rev.* B **40** 3066
[3] Kurita S, Haruki M and Miyagawa K 1987 *J. Phys. Soc. Japan* **57** 1789
[4] Haruki M and Kurita S 1989 *Phys. Rev.* B **39** 5706
[5] Donohoe R J, Ekberg S A, Tait C D and Swanson B I 1989 *Solid State Commun.* **71** 49
[6] Wada Y, Mitani T, Toriumi K and Yamashita M 1989 *J. Phys. Soc. Japan* **58** 3013

[7]	Bishop A R, Gammel J T and Phillpot S R 1989 *Synth. Met.* **29** F151
[8]	Ichinose S 1984 *Solid State Commun.* **56** 137
[9]	Onodera Y 1987 *J. Phys. Soc. Japan* **56** 250
[10]	Su W P, Schrieffer J R and Heeger A J 1979 *Phys. Rev. Lett.* **42** 1698; 1980 *Phys. Rev.* B **22** 2099
[11]	Takayama H, Lin-Liu Y R and Maki K 1980 *Phys. Rev.* B **21** 2388
[12]	Kawamori A, Aoki R and Yamashita M 1985 *J. Phys. C: Solid State Phys.* **18** 5487
[13]	Conradson S D, Stroud M A, Zietlow M H, Swanson B I, Baeriswyl D and Bishop A R 1988 *Solid State Commun.* **65** 723
[14]	Baeriswyl D and Bishop A R 1987 *J. Phys. C: Solid State Phys.* **21** 339
[15]	Liu J, Yang G X and Zhang D G 1990 *J. Phys.: Condens. Matter* **2** 6231
[16]	Liu J and Yang G X 1990 *Phys. Lett.* **147A** 301
[17]	Degiorgi L, Wachter P, Haruki M and Kurita S 1989 *Phys. Rev.* B **40** 3285
[18]	Phillpot S R, Rice M J, Bishop A R and Campbell D K 1987 *Phys. Rev.* B **36** 1735
[19]	Phillpot S R, Bishop A R and Horovitz B 1989 *Phys. Rev.* B **40** 1839
[20]	Gammel J T, Donohoe R J, Bishop A R and Swanson B I 1990 *Phys. Rev.* B **42** 10 566
[21]	Mishima A and Nasu K 1989 *Phys. Rev.* B **39** 5758; 5763
	Suzuki M and Nasu K *Preprint*
[22]	Sun X, Lu D, Fu R, Li X, Lin D L and George T F 1989 *Phys. Rev.* B **40** 12 446
[23]	Xing B and Sun X 1988 *Acta Phys. Sinica* **37** 507