

RESONANCE RAMAN SCATTERING AND INDUCED LATTICE RELAXATION
IN MIXED VALENCE CHAIN COMPOUND WOLFFRAM'S RED

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Raman scattering resonating to a charge transfer excitation in Wolfram's red is studied. Underneath a Raman line and its overtones polarized in chain direction (z) due to a vibration along the chain, a continuous z-polarized Raman-like emission is observed. It extends deeply into a band gap and is followed by a large z-polarized luminescence band. They are interpreted in terms of a recombination during and after a relaxation to a self-trapped state in a quasi-1-d mixed valence crystal.

I. Introduction

Wolfram's red is a mixed valence quasi-1-d semiconductor consisting of linear chains of $-\text{Pt}^{4+}-\text{Cl}^{-}-\text{Pt}^{2+}-\text{Cl}^{-}$ where Pt^{4+} and Pt^{2+} are each coordinated tetragonally by four ethylamines. The Cl^{-} in the chain is located closer to Pt^{4+} than to Pt^{2+} [1]. One might understand the structure of the chain by imagining a chain of $-\text{Pt}^{3+}-\text{Cl}^{-}-\text{Pt}^{3+}-\text{Cl}^{-}$. The highest band consisting of Pt $5d_{z^2}$ extending in the chain direction would be half-filled and Cl^{-} would be positioned at a middle point between platinum ions. However, this structure is unstable and is transformed into a Wolfram's red structure by performing a $2k_F$ Peierls transition accompanied by a localization of charge on alternate platinum ions and a displacement of chlorine ions from a middle point to double a periodicity. The structure could also be understood by supposing a charge transfer excitation from alternate Pt^{3+} to their neighbored Pt^{3+} , thus forming a $-\text{Pt}^{4+}-\text{Cl}^{-}-\text{Pt}^{2+}$ -excited chain. The excited states are then stabilized by a self-trapping, which always occurs in 1-d crystal [2], with a displacement of Cl^{-} to form a Wolfram's red structure. A charge transfer excitation of electron from Pt^{2+} to Pt^{4+} in Wolfram's red is just a reverse process of the above processes. The purpose of this work is to investigate this reverse process by measuring a Raman scattering resonating to the charge transfer excitation.

An optical absorption due to charge transfer excitation has been measured in Wolfram's red [3,4]. A resonance Raman scattering has been studied by CLARK et al. [4] who have found a Raman line and its overtones up to the 9th originating from a breathing vibration of Cl^{-} along the chain. Their measurement has been made, however, on un-oriented sample at room temperature and attention has been given to a resonance effect itself. In this study, we make an investigation at low temperature with taking account of a polarization and give a particular attention to a lattice relaxation process. We find a new type Raman-like emission as well as an ordinary Raman line and luminescence and they will be discussed in terms of a self-trapping in a quasi-1-d crystal.

II. Experimental Results

Single crystals of Wolfram's red were prepared by the method of REIHLEN and FLOHR [5]. Particular care was taken to maintain an incident laser power on sample being sufficiently low to avoid a decomposition and a heating of sample.

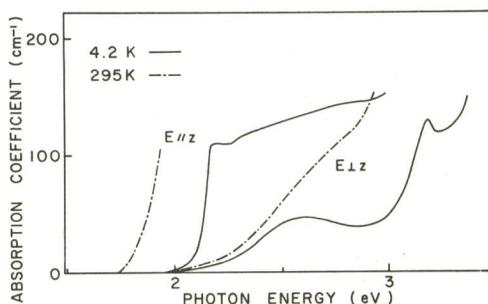


Fig.(1) Absorption spectra of Wolfram's red

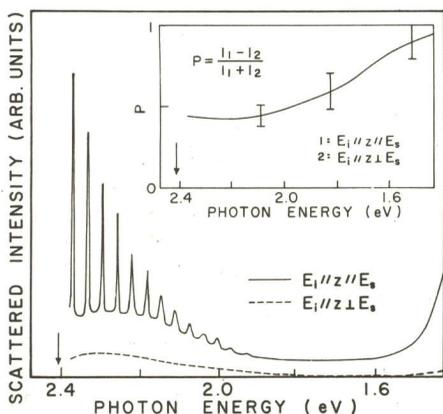


Fig.(2) Resonance Raman spectra excited at 2.409eV at 4.2K: In the inset, a degree of polarization of continuous band is shown. Arrows indicate exciting energies

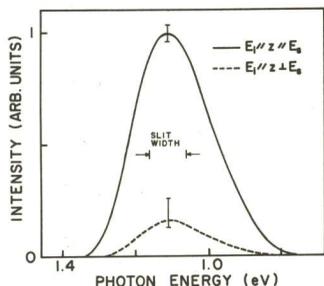


Fig.(3) Infrared emission band excited by light of $E_i // z$ at 2.409eV at 4.2K

Figure (1) is absorption spectra measured in this study. Here we take a direction of the chain as the z-direction. The spectrum at 4.2K is similar to that obtained previously [6]. It shows a flat absorption between 2.1 and 2.9eV with a small hump at 2.18eV at the edge when $E // z$. It is strongly polarized in the z-direction at the edge but is depolarized gradually as the energy increases. It has been assigned to a charge transfer excitation from a filled d_{z^2} of Pt^{2+} to an empty d_{z^2} of Pt^{4+} [3,4].

Figure (2) is Raman spectra at 4.2K excited at 2.409eV where light is absorbed by the charge transfer excitation. When $E_i // z // E_s$ where E_i and E_s are polarizations of incident and scattered light, a sharp Raman line of $308cm^{-1}$ ($38.2meV$) and its overtones up to the 14th are observed. Underneath the Raman lines, a continuous band is present which rises at the exciting energy and extends to lower energy deeply into a band gap. It is followed by a large infrared emission band shown in Fig.(3). In the spectrum of $E_i // z \perp E_s$ in Fig.(2), the $308cm^{-1}$ lines are hardly observed but the continuous band with small intensity is present so that the former is completely polarized but the latter is partially polarized in the z-direction. The infrared emission is polarized considerably in the z-direction. A degree of polarization, P, of the continuous band is shown in the inset of Fig.(2). We note that the degree of polarization increases gradually as the energy decreases and becomes high when the infrared emission sets in. When $E_i \perp z$, either the Raman lines or the continuous band as well as the infrared emission are exceedingly smaller than those for $E_i // z$. These fact would suggest that the above three emissions are

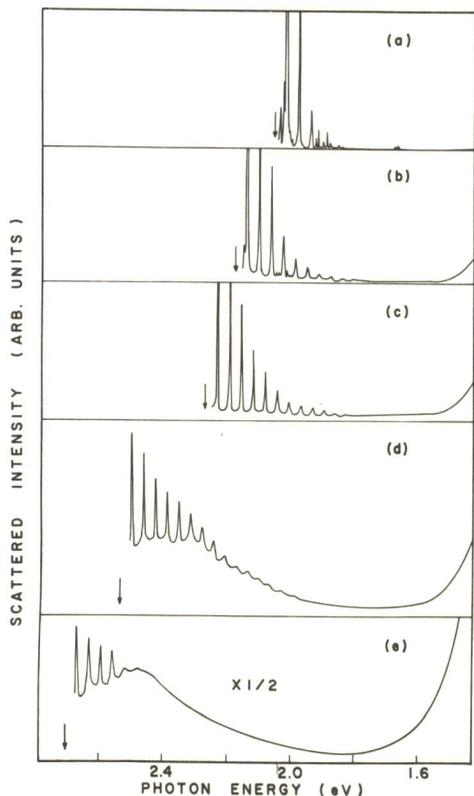


Fig. (4) Raman spectra for $E_i // z // E_s$ at 4.2K for different exciting energies; Arrows indicate exciting energies

We note that this breathing mode is an even parity longitudinal optical mode of $k=0$ of the chain.

It is believed that the ground state valence delocalization is quite small in Wolfram's red [6]. Thus holes left at Pt^{2+} sites after the charge transfer excitation would be localized. Excited electrons, however, would be delocalized somewhat in an empty narrow band associated mostly with d_{z^2} of Pt^{4+} , because the shape of the charge transfer absorption in Wolfram's red is not of Gaussian but is flat extending to high energy. In 1-d crystal, a band electron state is unstable and electron is always self-trapped by deforming a lattice due to an electron-phonon interaction [2]. In Wolfram's red, an electron excited by a charge transfer absorption will be finally localized at a Pt^{4+} site next to a Pt^{2+} site where a hole is localized by displacing a Cl^- towards a middle point between the above two platinum ions, thus forming possibly a $Pt^{4-\delta}-Cl^- - Pt^{3+}-Cl^- - Pt^{4-(1-\delta)}$ which is trapped in the original chain. By a recombination of electron and hole during this self-trapping process, light would be emitted although its intensity might be quite small. Its energy would be a function of a degree of relaxation and would decrease as a lattice relaxation proceeds. Thus the emission given off during a self-trapping would continue to low energy into a band gap because an

associated with $Pt^{2+}-Pt^{4+}$ charge transfer absorption.

Figure (4) shows how the spectrum for $E_i // z // E_s$ changes as an exciting energy varies. The spectrum (a) is an off-resonance spectrum. Here a prominent structure is a $308cm^{-1}$ Raman line and its 2-4 ω , and neither the continuous emission nor the infrared emission are found. When the exciting energy increases and reaches to a region where the charge transfer absorption sets in, the Raman lines of higher order and the continuous band as well as the infrared band appear. When the exciting energy increases further, the intensity of Raman lines decreases while the continuous band grows. The high energy edge of the continuous band moves with the exciting energy showing a Raman-like nature. The continuous band decreases its intensity at 80K and is fairly small at room temperature.

III. Discussion

The Raman line of $308cm^{-1}$ observed at 4.2K in the present work is a same line as was observed at $316cm^{-1}$ at room temperature and was assigned to a symmetric breathing mode of Cl^- around Pt^{4+} by CLARK et al. [4]. Our result of z-polarized nature of the excitation and of the scattered light support their interpretation.

adiabatic potential curve has no barrier in 1-d crystal. We propose, therefore, that the continuous Raman-like emission is an emission given off during the self-trapping. The decrease of the intensity of the overtone of 308cm^{-1} according to its order and the opposite dependence of the intensity of the Raman line on exciting energy to that of the Raman-like continuous emission would suggest a branching off of the self-trapping process from the Raman process. After the relaxation of lattice and the localization of electron are completed, an emission from the self-trapped state would be of usual Stokes-shifted Gaussian shape and the strong infrared emission at 1.1eV in Fig.(3) would be this emission. This interpretation would be supported by a strongly z-polarized nature of this emission which would be expected from the distribution of electron and hole localized along the chain in the self-trapped state.

The fact that the intensities of either the Raman lines or the Raman-like continuous band as well as the infrared emission by the excitation of $E_{i\perp z}$ relative to those of $E_{i\parallel z}$ are too weaker than those expected from the absorptions of $E_{\perp z}$ and $E_{\parallel z}$ would suggest that the resonating charge transfer excited state would be strongly z-polarized and the absorption found for $E_{\perp z}$ would not be associated with it. If this interpretation is correct, the following picture can be deduced to describe the experimental result of the continuous emission: At the beginning of the relaxation to the self-trapped state, the electronic state becomes more 3-d like possibly due to a mixing of some other state like other d state due to electron-phonon coupling. When the relaxation proceeds, electron is more localized on the chain, leading to a higher degree of polarization of an emission at lower energy, as we find in the inset of Fig.(2). This interpretation is, however, our speculation and further experimental evidence and more detailed analysis are needed to get a complete picture.

In conclusion, we say that the whole spectra we have observed in Wolfram's red can be explained in terms of a Raman effect and a recombination during and after the relaxation to a self-trapped state in quasi-1-d electron phonon system. Our spectra would be a direct experimental evidence to show a whole process of self-trapping which has not been clarified yet.

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