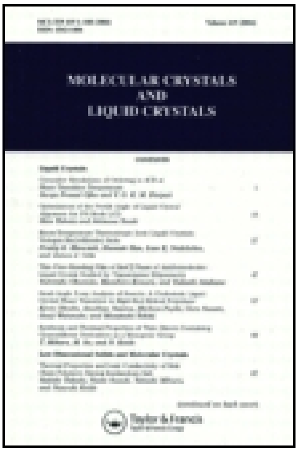

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Spectroscopic Study of Fluctuations of Kinks Photoinduced in an MX Chain Complex

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SPECTROSCOPIC STUDY OF FLUCTUATIONS OF KINKS PHOTOINDUCED IN AN MX CHAIN COMPLEX

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Abstract We report the experimental results on the temperaturte dependence of the photoinduced midgap absorption bands in $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$. The behaviors of the spectral position and line shape of the A band are found to be explained well in terms of the quantum fluctuation and translational motion of solitons.

INTRODUCTION

Among many mixed-valence MX chain complexes, it is only the substance $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ (en=ethylenediamine) that has been verified by the photoinduced electron paramagnetic resonance (EPR) to support long-lived, mobile spin solitons.[1] The unpaired electron is confined in a segment Pt-Cl-Pt of the MX (M=Pt, X=Cl) chain. The EPR spectrum shows that the spin density at the two Pt sites of this segment is fluctuating significantly even at liquid He temperatures.[2] The EPR spectrum, however, gives little information about the origin of the fluctuation.

In the present work, to distinguish between the static disorder and quantum fluctuation effects, we study the temperature dependence of the midgap optical absorption band induced by laser-irradiation. We show that the experimental results are explained well on the basis of a quantum fluctuation model.

EXPERIMENTAL RESULTS

Single crystals with a thickness of 50-100 μm are irradiated by the 488 nm line of an Ar-ion laser at 200 K. In order that the midgap states are created homogeneously throughout the crystal, the laser is polarized **E⊥b**, where **E** and **b** are the electric field of light and the chain axis, respectively. The laser is turned off after the sample is irradiated up to a given fluence. Afterward, the absorption spectrum is measured in a temperature range between 10 K and 200 K.

The induced absorption persists as long as temperature is kept below 200 K, the irradiation temperature. Figure 1 shows the spectrum for **E** || **b** at various temperatures. As shown by the spectrum (a) in Fig.1, all the intragap absorption bands A, B and B' appearing below the edge of the charge-transfer band CT are very weak before irradiation, demonstrating good quality of the sample. Interestingly, the A band has an asymmetric line shape, showing a greater width on the higher energy side. Moreover, its peak position shifts toward higher energies as temperature increases.

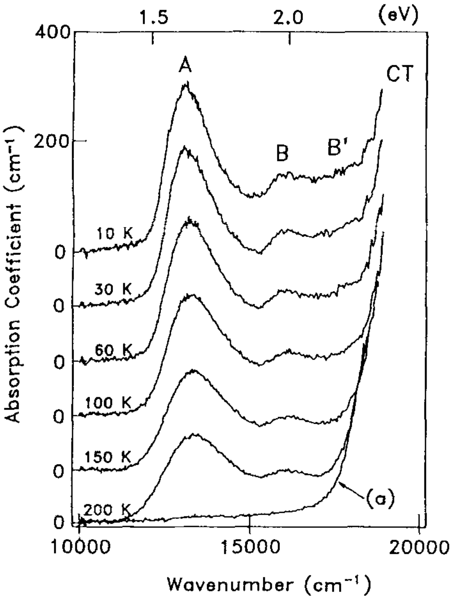

FIGURE 1. Near infrared absorption spectrum taken at various temperatures after the sample is irradiated by the 488 nm line of an Ar-ion laser at 200 K. The curve (a) is the spectrum taken at 200 K prior to the irradiation.

To see the variation of the spectrum quantitatively, we decompose the observed spectrum by using the log-normal function[3] for A and B' bands, and Gaussian function for the edge of the CT band; the B band is much weaker than the A and B' bands and the asymmetry seems subtle, so that Gaussian is used to fit the B band.

Figure 2 shows an example of the least-squares curvefit obtained by an iteration method, which is in excellent agreement with the data. As shown in Fig.2, the asymmetry of a log-normal spectrum is expressed by a parameter ρ: As $\rho \rightarrow 1$, the line shape approaches a Gaussian. The value of ρ of the A band amounts to 1.6 at 10 K; it decreases monotonically with increasing temperature to reach 1.2 at 200 K. The peak position ν_0, on the other hand, of the A band turns out to shift from 1.62 eV at 10 K toward 1.65 eV at 200 K.

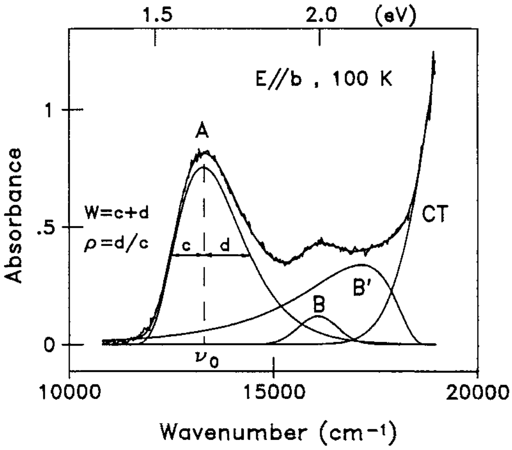

FIGURE 2. Least-squares curvefit to the photoinduced absorption spectrum at 100 K. The smooth line on the experimental spectrum is the result of the curvefit. ν_0 is the peak position and *c* and *d* are the half-maximum widths of the log-normal function.

In the present article, we focus our attention on the behavior of the A band. As will be shown later, *n*th moments of the absorption spectrum reflect the dynamical properties of a localized center well. First moment, i.e., the mean energy ν_m, second moment μ_2, and third moment μ_3 of an absorption band $A(\nu)$ are defined as follows;

$$\nu_m = \frac{1}{\mathcal{A}} \int_0^\infty \nu A(\nu) d\nu \tag{1}$$

$$\mu_2 = \frac{1}{\mathcal{A}} \int_0^\infty (\nu - \nu_m)^2 A(\nu) d\nu \tag{2}$$

$$\mu_3 = \frac{1}{\mathcal{A}} \int_0^\infty (\nu - \nu_m)^3 A(\nu) d\nu \ , \tag{3}$$

where ν denotes photon energy, and $\mathcal{A} = \int_0^\infty A(\nu)d\nu$. The log-normal function enables us to evaluate these moments analytically.[4] Figure 3 shows the temperature dependencies, obtained from the present experiment, of ν_m, μ_2 and μ_3 of the A band.

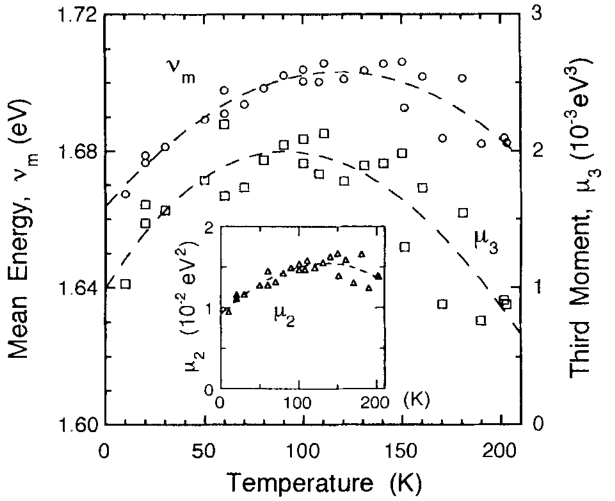

FIGURE 3. Temperature dependencies of ν_m (○), μ_2 (△) and μ_3 (□) of the A band. Dashed lines are drawn as guides.

DISCUSSION

The intragap absorption bands observed are considered to arise from either solitons or polarons. All the theories available at present show that in the MX chain complexes the intensity of an intragap absorption band due to a polaron, if it exists in the crystal, should be comparable to that due to a soliton.[5,6,7] As already mentioned, however, EPR experiments have proved that, compared to the number of spin solitons, only a very few paramagnetic polarons can be photoinduced in the present substance.[1] It is natural, therefore, to attribute the A, B and B' bands to solitons.[8]

We see from Fig.3 that at 10 K both the quantities $\sqrt{\mu_2}$ and $\sqrt[3]{\mu_3}$ amount to 0.10 eV=1160 K. Another remarkable aspect of our experimental result is that not only μ_2 but also ν_m and μ_3 increase with increasing temperature from 10 K up to about 100 K; the increase in ν_m, $\sqrt{\mu_2}$ and $\sqrt[3]{\mu_3}$ amounts to 0.034 eV=390 K, 0.028 eV=320 K and 0.026 eV=300 K, respectively. Static disorder of the photoinduced solitons as observed by a resonance Raman experiment[9] may give rise to some extent of inhomogeneous broadening. Though this broadening would contribute to μ_2 and μ_3, it must be rather independent of temperature. Therefore, the static disorder effect is likely irrelevant to the present result. Furthermore, since the CT absorption peak shifts toward lower energies with increasing temperature,[10] the behavior of ν_m between 10 K and 100 K can not be ascribed to the thermal change of the energy gap.

In principle, the adiabatic potential energy of a soliton is not uniform. This is shown schematically in Fig.4. If a soliton is bound by one of the wells of the potential, it would perform a quantum vibration, of which the frequency depends on the effective soliton mass[11,12] as well as the depth of the well. It is known that the zero-point motion of a localized center causes the absorption band to have a large damping and asymmetry even at very low temperatures.[13] Siano and Metzler[14] have treated the *n*th moments in a harmonic approximation. According to their theory, thermal enhancement of the vibrational motion may raise the value of μ_2 significantly. Their theory shows further that the crucial factor for determining the values of ν_m and μ_3 is the vibrational frequency, ω_e, of the excited state relative to the frequency, ω_g, of the ground state. Namely, the sign of μ_3 and the temperature coefficients of ν_m and μ_3 are all positive if $\omega_e > \omega_g$, whereas they are negative if $\omega_e < \omega_g$. Given that $\omega_e > \omega_g$, the quantum fluctuation model is quite consistent with our experimental result.

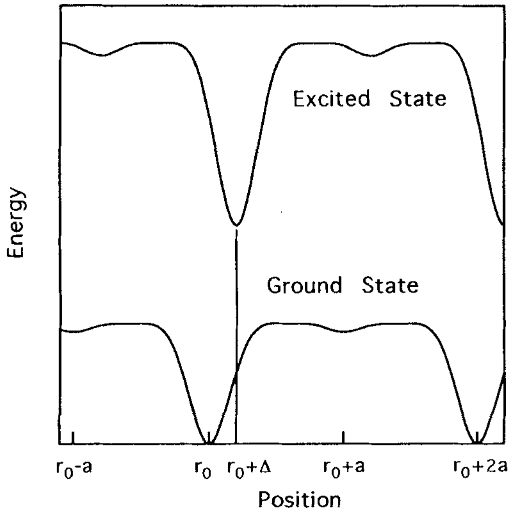

FIGURE 4. A model of the ground and excited state potentials as a function of the position in an MX chain. r_0 refers to an equilibrium position, a to the nearest Pt-Pt distance, and Δ to the relative displacement of the potential minima.

We note in Fig.3 that around 100 K, ν_m, μ_2 and μ_3 begin to decrease with increasing temperature. This fact reminds us that, if a soliton is unbound, the absorption band should be ordinarily narrow;[6,7] moreover ν_m must follow half the energy gap upon a change in temperature,[11] and therefore must decrease as temperature increases. Consequently, our experimental result is reasonable given that above about 100 K the soliton spends an appreciable time at unbound positions (see Fig.4) as a result of thermal excitation from the bound state. Indeed, the activation energy for the translational motion of spin solitons is known to be 11-13 meV=130-150 K,[15,16] suggesting that the A band originates mainly from spin solitons.

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