

## Pressure-Induced Continuous Phase Transition of Charge-Density-Wave State in a Linear-Chain Complex

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[Pt(en)<sub>2</sub>][Pt(en)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (en=ethylenediamine) is found to undergo a novel phase transition from the charge-density-wave (CDW) state to a new phase under hydrostatic pressure. The new phase appears at 3 GPa and coexists with the CDW state up to 6 GPa, at least. The volume ratio between the two coexisting phases measured by Raman scattering spectroscopy changes continuously with pressure. The result is discussed in terms of the theoretical approach to the polymorphic phase transition developed recently by Bassler, Sasaki, and Griffiths. It is suggested that kink solitons play an important role in this phase transition.

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In halogen-bridged linear-chain complexes of platinum and palladium, a strong electron-lattice coupling causes the valence of metal ions to form a charge-density-wave (CDW) state in the way of  $-X-M^{II}-X-M^{IV}-$  [1], where  $X$  and  $M$  denote halogen and metal ions, respectively. Many materials of this family exhibit the order of the CDW state in one dimension only, since the interchain interaction is very weak [2,3]. In this Letter, we report the first observation of the pressure-induced phase transition of the quasi-one-dimensional CDW state in the platinum complex [Pt(en)<sub>2</sub>][Pt(en)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>, where en denotes ethylenediamine. So far, orthorhombic (CDW-I) and monoclinic (CDW-II) phases are known in this material [3,4]. We have found that the CDW-II phase transforms continuously to a new ordered phase in an unusual way: The new phase appears at 3 GPa and coexists with CDW-II up to at least 6 GPa, the highest pressure examined. This coexistence does not seem to be an ordinary coexistence at a first-order phase transition. We show that this novel phase transition can be described well in terms of the phenomenological theory developed recently by Bassler, Sasaki, and Griffiths [5].

We study the pressure dependence of the Raman scattering and optical absorption spectra in single crystals by the use of microscope-spectrometer systems equipped with a diamond anvil apparatus [4,6]. We use Sumitomo 3M Fluorinert FC-75 or paraffin oil to produce a quasi-hydrostatic environment inside the pressure cell. The Raman scattering spectrum is measured in the back-scattering geometry with respect to the crystal surface containing the axis of the chainlike bonds, i.e., the  $b$  axis. The 488-nm line of an Ar ion laser is used as the light source for the excitation of the Raman scattering as well as the luminescence of  $R$  lines of ruby which is used to calibrate pressure. The absorption spectrum is measured with the incident light polarized parallel to the  $b$  axis, since both the charge-transfer and midgap bands on

which we focus our attention in the present study are allowed only for this polarization [4,6]. All the measurements are performed at room temperature.

Figure 1 shows the Raman scattering spectra in the range 200–400 cm<sup>-1</sup> of the Stokes shift at various pressures. If pressure exceeds 3 GPa, a new Raman line appears about 19 cm<sup>-1</sup> above the line due to the intrachain bond-stretching vibration of Cl ions of CDW-II [4]. The new line grows rapidly with pressure, while the intensity

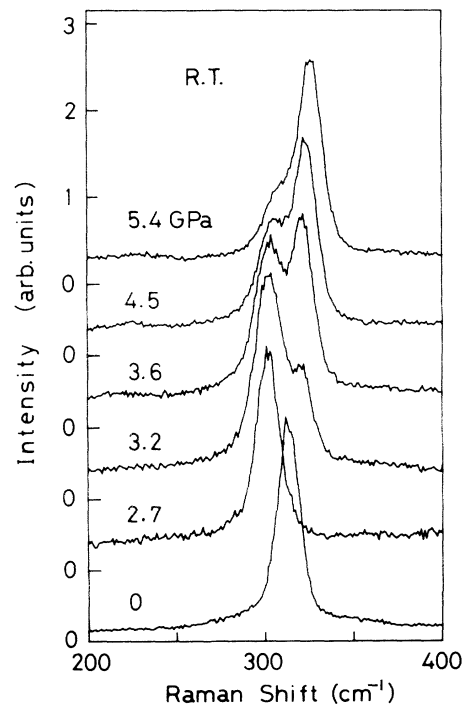


FIG. 1. Raman scattering spectra of the Pt-Cl stretching mode at various pressures.

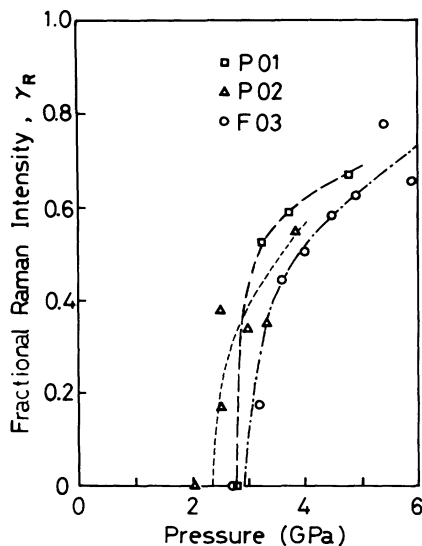


FIG. 2. Variation of the fractional intensity of the pressure-induced Raman line for several samples. The lines are drawn as a guide, indicating the general trend.

of the original line is reduced. Figure 2 shows the variation of the fractional intensity  $\gamma_R$  of the new line observed for several samples, where  $\gamma_R$  is defined by  $\gamma_R = I_1/(I_0 + I_1)$  with the intensities  $I_0$  and  $I_1$  of the original and the new lines, respectively. The rate of growth of the new line decreases with increasing pressure, so that  $\gamma_R$  amounts to only about 0.7 even at 6 GPa. The spectral locations of both lines shift smoothly as pressure increases up to 6 GPa, while keeping the spacing between the two lines nearly constant. Our experiment suggests that the spectrum changes reversibly upon a decrease of pressure [7]. In view of these changes in the spectrum, the system is likely in thermal equilibrium at any pressure.

At low pressures, the sample observed under the microscope with the  $E_{11b}$  polarization is transparent for orange light. As pressure approaches 3 GPa, the sample becomes dark red, and eventually opaque because the charge-transfer band shifts towards lower energies and the midgap bands due to kink solitons [4,6,8] become intense. The sample becomes dark red again around 3.5 GPa, and then recovers transparency notably as pressure increases further. Figure 3 shows this change by the absorption spectra obtained with a spatial resolution of 50  $\mu\text{m}$  in diameter. Under pressures above about 4 GPa, the degree of transparency is noted to be somewhat inhomogeneous, so that the sample looks like a mosaic. The spectrum at 4.8 GPa in Fig. 3 is taken from the area covering many portions of the mosaic. To clarify the reason for the recovery of transparency, we have measured the absorption spectra with a higher spatial resolution, i.e., 20  $\mu\text{m}$  in diameter. The inset of Fig. 3 shows the spectra obtained at 4.1 GPa for the most opaque area and the clearest one. Obviously, the spectral positions of the

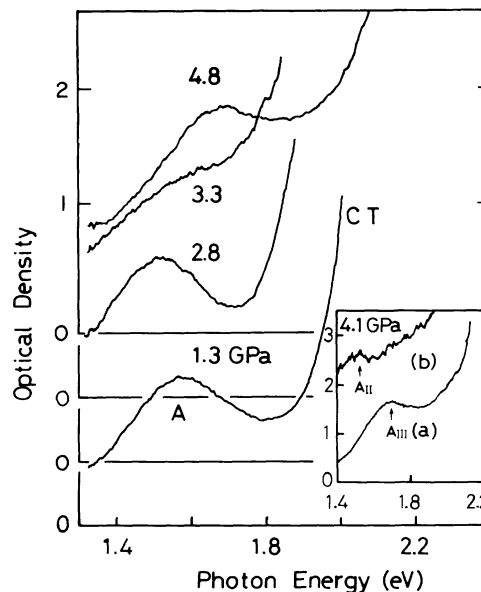


FIG. 3. Absorption spectra for  $E_{11b}$  at various pressures. The absorption bands denoted by  $A$  and  $CT$  are the midgap and the charge-transfer bands, respectively. The base line is shifted upward in the increasing order of pressure. Inset: Spatially resolved spectra obtained at 4.1 GPa for (curve  $a$ ) the clearest and (curve  $b$ ) the most opaque area of a sample.  $A_{II}$  and  $A_{III}$  are the midgap bands of CDW-II and CDW-III phases, respectively.

charge-transfer and the midgap bands are different for the two spectra. This result shows that the recovery of transparency is due to the growth of a new phase, say CDW-III, of which the fundamental energy gap is greater by 0.3–0.4 eV than that of CDW-II. Correspondingly, the midgap band of CDW-III appears at a photon energy which is 0.15–0.2 eV higher than that of CDW-II.

The evolution of the contribution from the CDW-III phase to the absorption spectrum is correlated well with the evolution of the new Raman line. Therefore, we attribute the new Raman line to a bond-stretching mode of Cl ions in the CDW-III phase. It is worth noting that the CDW-III phase has a steep tail of the charge-transfer band and a distinct midgap absorption band. Moreover, the Raman line of CDW-III is as narrow as that of CDW-II at any pressure. In the light of the site-diagonal electron-lattice coupling [1] peculiar to the present material, these facts strongly suggest that the CDW-III phase is a periodically ordered state of Pt and Cl ions as well as CDW-II, and that the domain sizes of the coexisting phases are much larger than the lattice constant.

To examine the uniformity of pressure above 4 GPa, we have measured the Raman scattering by focusing the laser beam on various places of the pressurized sample with a spot size of 10  $\mu\text{m}$  in diameter. The spectrum

turns out to exhibit the doublet features regardless of place; their spectral positions remain almost unchanged, though the relative intensities depend on the place. These results confirm that pressure itself is rather uniform, and the CDW-II and CDW-III phases coexist everywhere in the micrometer scale of dimension.

How can the two phases coexist over such a wide range, more than 3 GPa, of pressure? In a first-order phase transition, two phases coexist only at the transition point. Irregularity of pressure in the sample may result in the coexistence over a finite range of pressure, but this possibility is ruled out by the present experimental analysis. The reversible change in the Raman spectrum also suggests that what we have observed is not a first-order coexistence.

Two-phase coexistence over wide ranges of temperature and pressure is observed also in neutral-to-ionic transitions of some mixed-stack organic complexes such as TTF-chloranil [9]. Hubbard and Torrance [10] have modeled the coexistent state into a superlattice of neutral and ionic lattice planes: The ionized plane is considered as a defect which is introduced to the array of neutral planes. In this model, the length of the domain of one phase is a constant of the order of the lattice constant, while that of the other phase varies with model parameters. In the present material, however, the domain sizes of both CDW-II and CDW-III are likely to be much greater than the lattice constant as argued above. In this situation, it seems unnatural to assume the domain size of only CDW-II to be variable under pressure, while considering the domain of CDW-III as a defect. Therefore, we think it is appropriate to extend the model, to account for what we have observed, in such a way that the domain sizes of both coexisting phases can be varied. A relevant model has recently been studied theoretically by Bassler, Sasaki, and Griffiths [5], independent of any experiment. In the following, we show that the observed behavior of  $\gamma_R$  can be well described in terms of this theory.

Let us consider a single long chain consisting of a sequence of the domains of CDW-II and CDW-III phases. Let the lengths of the  $i$ th domains of CDW-II and CDW-III be  $l_i$  and  $m_i$ , respectively, in units of a Pt-Cl-Pt bond. Then, the total free energy  $f$  per bond of the chain can be written as

$$f = \frac{\sum_i \{2\sigma + l_i \varepsilon_{II} + m_i \varepsilon_{III} + \phi_{II}(l_i) + \phi_{III}(m_i)\}}{\sum_i (l_i + m_i)}, \quad (1)$$

where  $\sigma$  is the creation energy of an interface,  $\varepsilon_{II}$  and  $\varepsilon_{III}$  are free energies per bond of CDW-II and CDW-III, respectively, and  $\phi_{II}(l_i)$  and  $\phi_{III}(m_i)$  are the interaction energies between interfaces holding the  $i$ th domains of CDW-II and CDW-III, respectively. [As is apparent from Eq. (1), the present model is reduced to Hubbard and Torrance's defect model provided  $m_i$  and  $\phi_{III}(m_i)$  are constant.] We choose the following simple power functions for the repulsive interactions:  $\phi_{II}(l_i) = Al_i^{-a}$  and

$\phi_{III}(m_i) = Bm_i^{-a}$ , where  $A$ ,  $B$ , and  $a$  are positive constants. The thermal equilibrium state is given by a set of integers  $l_i$  and  $m_i$  which minimizes  $f$ . The mixed-phase states turn out to exist when  $\sigma < 0$  and the quantity  $\varepsilon = \varepsilon_{II} - \varepsilon_{III}$  is in the range  $\varepsilon_1 < \varepsilon < \varepsilon_2$ , as schematically illustrated in the inset of Fig. 4. Note that the values of  $\varepsilon_1$  and  $\varepsilon_2$  depend on  $\sigma$ ,  $a$ ,  $A$ , and  $B$ .

We interpret that the parameter  $\varepsilon$  increases with pressure  $P$ , and crosses the boundary  $\varepsilon = \varepsilon_1$  at the critical pressure  $P_1 \approx 3$  GPa (the process is indicated by the bold, upward arrow in the inset of Fig. 4). The variation of  $\varepsilon$  under pressure can be expressed as  $-(P - P_0)\delta V$ , where  $-P_0\delta V$  is the work to be done by pressure to induce the volume change  $\delta V$  per Pt-Cl-Pt bond upon the transformation from CDW-II to CDW-III at pressure  $P_0$  where  $\varepsilon = 0$ . Thus, we have

$$\varepsilon - \varepsilon_1 = -(P - P_1)\delta V. \quad (2)$$

By treating  $l_i$  and  $m_i$  as continuous variables, the mole fraction  $\gamma_M = \sum_i m_i / \sum_i (l_i + m_i)$  of the CDW-III phase is obtained as  $\gamma_M \propto (\varepsilon - \varepsilon_1)^{1/a}$  for  $\varepsilon$  just above  $\varepsilon_1$ . Hence, Eq. (2) gives

$$\gamma_M \propto (P - P_1)^{1/a}, \quad (3)$$

for  $P \gtrsim P_1$ .

The fractional intensity  $\gamma_R$  shown in Fig. 2 can be regarded as a measure of  $\gamma_M$ . The experimental results of  $\gamma_R$  demonstrate the behavior expected from Eq. (3) for  $a > 1$ . The theoretical value of  $\gamma_M$  in the whole region of pressure is obtained by numerically solving the equations  $\partial f / \partial l_i = \partial f / \partial m_i = 0$ . We now have three adjustable parameters,  $a$ ,  $r$ , and  $p$ , where  $r = \sqrt{B/A}$  and

$$p = 2a\sigma\{(1+a)\delta V\}^{-1}[-2\sigma\{(1+a)rA\}^{-1}]^{1/a}.$$

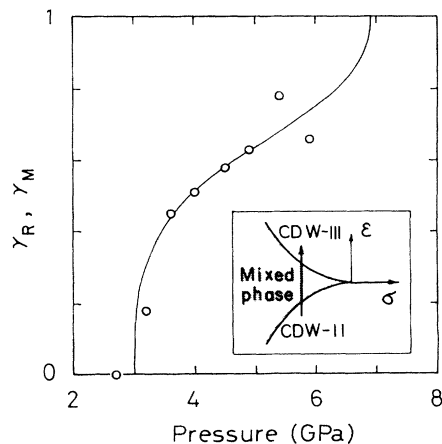


FIG. 4. A comparison between  $\gamma_R$  (open circles) of the sample F03 and a theoretical curve of  $\gamma_M$  (solid line) calculated with  $a=2.0$ ,  $r=1.6$ , and  $p=1.9$  GPa. Inset: Schematic phase diagram in the  $\sigma\varepsilon$  space, in which the bold, upward arrow indicates a trajectory traced by the sample as pressure increases.

Good agreement between the calculated curve of  $\gamma_M$  and experimental values of  $\gamma_R$  can be obtained with  $a=2-3$ ,  $r=1-2$ , and  $p=1.3-2.0$  GPa. Figure 4 shows a comparison of the calculated curve and the experimental results.

In order to estimate the interface energy  $\sigma$ , we need to know the values of  $\delta V$  and  $A$  as well as those of  $a$ ,  $r$ , and  $p$  deduced from the above analysis. The change in the crystal volume accompanied by the present phase transition is too small to be measured by observing the crystal under optical microscope, so that the magnitude of  $\delta V$  is presumably smaller than 3% [11]. The fact that the domain lengths are sufficiently larger than the lattice constant implies  $A \gg |\sigma|$ . Then, assuming that the value of  $A$  is an order of magnitude larger than  $|\sigma|$ , we obtain  $-\sigma \lesssim 0.3$  eV, which seems reasonable compared with the electron-lattice coupling energy of 1.5–1.8 eV per Pt-Cl-Pt bond [4,12].

If our interpretation is correct, then what is the mechanism to produce negative  $\sigma$ ? An interesting phenomenon which might be connected to this fundamental problem shows up in Fig. 3: The density of solitons as manifested by the intensity of the midgap absorption band becomes very high in the CDW-II phase under high pressures; the CDW-III phase also exhibits an intense midgap band. As far as the CDW-II phase is concerned, the soliton is an antiphase domain wall with a formation energy of about 1 eV [1,12]. Our observation leads us to imagine that, with increasing pressure, some of the CDW-II domains are transformed to the CDW-III domains; the solitons between transformed and untransformed domains are converted into interfaces, accordingly. We conjecture that the interface has a lower formation energy than the soliton, and therefore the net energy, i.e.,  $\sigma$ , needed to create an interface is negative. The formation energy of an interface between neutral and ionized domains in TTF-chloranil is also conceived to be small [13].

The close resemblance between the optical spectra of CDW-III and those of CDW-II suggests that the CDW-

III phase is a modification of CDW-II. At present, however, we cannot rule out other possibilities such as the bond-order-wave state [1]. In any case, detailed structural studies under high pressure are strongly desirable to clarify the microscopic mechanism of this novel phase transition unambiguously.

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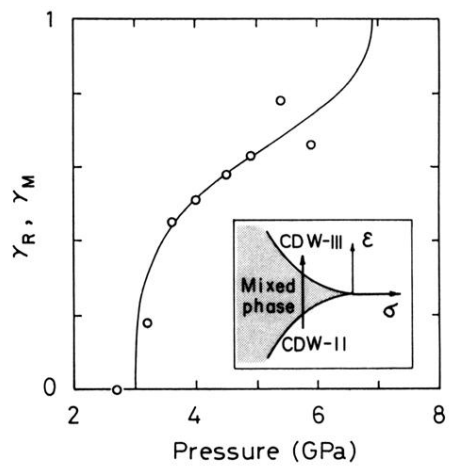


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