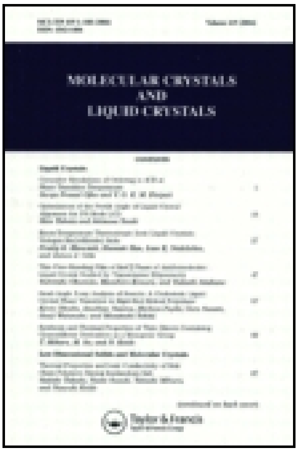

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Pressure Effects on Quasi-One-Dimensional Mixed-Valence Gold Complex $[AuCl(DBS)][AuCl_3(DBS)]$ (DBS = dibenzylsulfide)

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Effects of hydrostatic pressure have been investigated in a quasi-one-dimensional (quasi-1D) mixed-valence (MV) gold complex $[AuCl(DBS)][AuCl_3(DBS)]$ (DBS=dibenzylsulfide) by means of high pressure Raman spectroscopy up to ~13 GPa at 300 K. We have observed pressure-induced suppression of a Raman-active Au-Cl stretching mode, indicating a precursor of the pressure-induced phase transition from the MV state to a single-valence (SV) state.

Keywords: valence disproportion; phase transition; pressure-effect; Raman spectroscopy; quasi-one-dimensional system

INTRODUCTION

Mixed-valence metal complexes have been attracting current interest due to their characteristic physical properties[1]. Especially, in the gold complex $Cs_2Au_2X_6$ (X=Cl, Br, and I) with three-dimensional Au-X network[2], the strong electron-lattice coupling induces alternation of the monovalence (Au^+) and trivalence (Au^{3+}) states, or the mixed-valence (MV) state. The MV state is transformed into the single-valence (SV) state with only Au^{2+} ions under a pressure of ~12 GPa for X=Cl and ~7 GPa for X=Br, respectively[3]. In accord with the MV-SV phase transition, the electrical resistivity of $Cs_2Au_2Cl_6$ decreases from ~10^6 Ωcm at ambient pressure to ~10^{-3} Ωcm at ~11GPa[4], indicating that the high-pressure SV phase is metallic.

[Au*X*(DBS)][AuX_3(DBS)] (*X*=Cl and Br, DBS=dibenzylsulfide) is another candidate that shows a similar pressure-induced MV to SV phase transition. In this system, Au ions take two valence states, i.e., Au^+ and Au^{3+}, which form neutral Au*X*(DBS) and AuX_3(DBS) molecules[5]. These two kinds of molecules align alternately along the *a*-axis, forming a gold-halogen chain: $\cdots X^- - Au^{3+} - X^- \cdots Au^+ \cdots X^- - Au^{3+} - X^- \cdots$ [5]. In the chain, the halogen ions are closer to the Au^{3+} sites. Interrante *et al* [6]. investigated pressure dependence of the resistivity for [AuCl(DBS)][$AuCl_3$(DBS)] up to ~30 GPa, and observed a minimum of resistivity at ~20 GPa, which is analogous to that for $Cs_2Au_2Cl_6$ at ~11GPa[4], where a MV to SV phase transition takes place. This observation suggests a possible pressure-induced phase transition into the SV state, i.e., $\cdots Cl^- \cdots Au^{2+} \cdots Cl^- \cdots Au^{2+} \cdots Cl^- \cdots Au^{2+} \cdots Cl^- \cdots$. Recently, Liu *et al* [7]. reported a pressure-induced MV to SV phase transition in [AuBr(DBS)][$AuBr_3$(DBS)] at ~8 GPa by means of high-pressure Raman spectroscopy.

In this paper, we have investigated the pressure effects on [AuCl(DBS)][$AuCl_3$(DBS)] in the pressure region up to ~13 GPa by means of high-pressure Raman spectroscopy. We have observed suppression of a Raman active Au-Cl stretching mode. By extrapolating the Raman data, the critical pressure for the MV to SV phase transition is estimated to be ~17 GPa. We further discussed the pressure-induced Fermi resonance effect on the Au-Cl stretching modes.

EXPERIMENTAL

The complex [AuCl(DBS)][$AuCl_3$(DBS)] was synthesized using a method reported in Reference 5. Single crystals were recrystallized from a chloroform solution at 278 K for four weeks. Thus obtained samples were orange needle-shaped. The needle direction is parallel to the crystallographic *a*-axis. The high-pressure Raman measurements were performed at 300 K using a diamond anvil cell with liquid paraffin as a pressure medium. A tiny crystal was placed in the gasket hole (0.3 mm in diameter). The magnitude of the applied pressure was monitored with the luminescence from a small piece of ruby placed in the gasket hole. The sample was excited at 514.5 nm with an Ar^+ laser in a backward configuration. To avoid the sample damage, the laser power density was kept below 35 W/cm^2. Scattered light was detected with a double monochromator equipped with a photoncounting system. To assign the Au-Cl stretching vibration of [AuCl(DBS)][AuCl$_3$(DBS)], we synthesized molecular crystals of AuCl(DBS) and AuCl$_3$(DBS) using the methods reported in References 8 and 9, respectively, and measured the Raman spectra.

RESULTS AND DISCUSSION

Before describing details of pressure effects on the Raman spectra in [AuCl(DBS)][AuCl$_3$(DBS)], let us survey the variation of the Raman selection rule at the expected MV-SV phase transition. In the MV phase, both the AuCl(DBS) and AuCl$_3$(DBS) molecules have site symmetry C_{2v}. Then, enumeration of the Au-Cl stretching modes for the AuCl(DBS) molecule is A_1, and that for the AuCl$_3$(DBS) molecule is $2A_1+B_1$. All the modes are Raman-active. On the other hand, in the postulated SV state, i.e., when the Cl^- ions locate at the central position between the two nearest neighboring Au sites along the chain, enumeration of the Au-Cl stretching modes gives A_1+B_1. *Therefore, two Raman-active A_1 modes should disappear in the SV phase.*

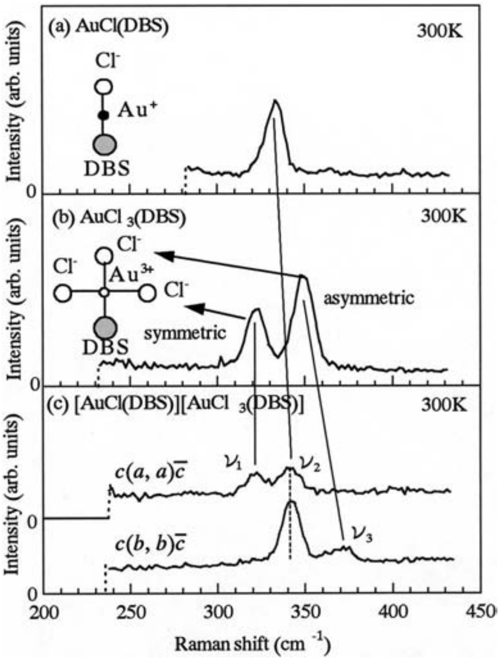

FIGURE 1 Raman spectra of (a) AuCl(DBS), (b) AuCl$_3$(DBS) and (c) [AuCl(DBS)] [AuCl$_3$(DBS)] at 300K. Inset shows respective schematic structures.

Figure 1(a) and (b) show the Raman spectra of AuCl(DBS) and AuCl$_3$(DBS) crystals at 300K, respectively. Two Raman-active bands (one Raman-active band) are observed at 323 cm^{-1} and

348 cm^{-1} (at 335 cm^{-1}) due to the Au-Cl stretching vibrations in $AuCl_3$(DBS) [AuCl(DBS)]. Judging from the lengths of the Au-Cl bond in the $AuCl_3$(DBS) molecule[10], the lower-lying band (at 323 cm^{-1}) is ascribed to the symmetric vibration, while the higher-lying one (at 348 cm^{-1}) is due to asymmetric one. (see Figure 1(b)) The symmetric (asymmetric) vibration corresponds to the Au-Cl vibration along (perpendicular to) the Cl-Au-Cl direction. Figure 1(c) shows polarized Raman spectra of [AuCl(DBS)][$AuCl_3$(DBS)]. Three Raman-active A_1 modes are observed at 320 cm^{-1} (ν_1), 340 cm^{-1} (ν_2) and 370 cm^{-1} (ν_3). If we compare frequencies of these modes (ν_1, ν_2, and ν_3) with those observed in AuCl(DBS) (Figure 1(a)) and $AuCl_3$(DBS) (Figure 1(b)), we can assign them to the respective intramolecular Au-Cl stretching modes of the AuCl(DBS) and $AuCl_3$(DBS) molecules. Among the three A_1 modes, the symmetric mode (ν_1; 320 cm^{-1}) of the $AuCl_3$(DBS) molecule should disappear in the postulated SV state[7].

Figure 2 shows variation of the unpolarized Raman spectra for [AuCl(DBS)][$AuCl_3$(DBS)] against pressure at 300 K. Under a pressure of 1.8 GPa, three Raman bands (ν_1, ν_2, and ν_3) are observed. With increasing pressure, the intensity of the ν_1 band decreases, while the ν_2 and ν_3 bands seem to converge into a single band. We have decomposed the spectra into three (or two) Lorentz components. Thus obtained intensity of the ν_1 mode and frequencies of the three modes are plotted against pressure in Figure 3(a) and (b), respectively. As shown in Figure 3(a), the intensity of the ν_1 mode shows a significant pressure-induced suppression around ~8 GPa, suggesting a possible MV-SV transition. Note that the ν_1 mode should disappear in the SV phase. A similar pressure-induced suppression of the ν_1 mode has been reported for [AuBr(DBS)][$AuBr_3$(DBS)] [7]. With

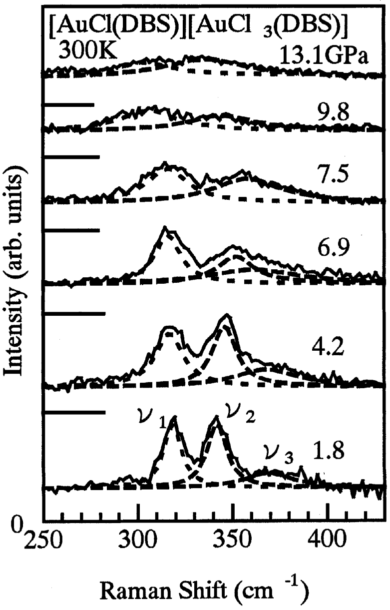

FIGURE 2 Pressure dependence of unpolarized Raman spectra for [AuCl(DBS)][$AuCl_3$(DBS)] at 300K.

linearly extrapolating the intensity data above 8 GPa (dotted line in Figure 3(a)), we roughly estimate the critical pressure P_c for the MV-SV phase transition to be ~17 GPa (downward arrow). Thus estimated P_c is close to ~20 GPa, where the resistivity shows a minimum[6]. In addition, application of pressure induces a softening (-0.9 cm^{-1}/GPa) of the ν_1 mode, as indicated by squares in Figure 3(b). The softening suggests elongation of the Au-Cl bondlength and resultant weakening of the bond along the chain, which is consistent with the expectation of the pressure-induced MV to SV phase transition. A similar pressure-induced softening (-2.3 cm^{-1}/GPa) of the ν_1 mode was reported for *X*=Br compound[7].

As shown in Figure 3(b), the ν_2 (ν_3) mode, which is ascribed to asymmetric Au-Cl stretching vibration perpendicular to the chain direction, shows a pressure-induced hardening (softening) behavior. (see circles in Figure 3(b)) At ~7.5 GPa, the two modes apparently converge into a single band. (also see Figure 2) With further increase of pressure beyond ~7.5 GPa, the spectral weight of the ν_2 mode seems to be suppressed. Such a suppression of the spectral weight can be ascribed to the Fermi resonance[11]. Recall that the ν_2 and ν_3 modes have the same symmetry (A_1) and can be mixed if their frequencies are close. Here, the

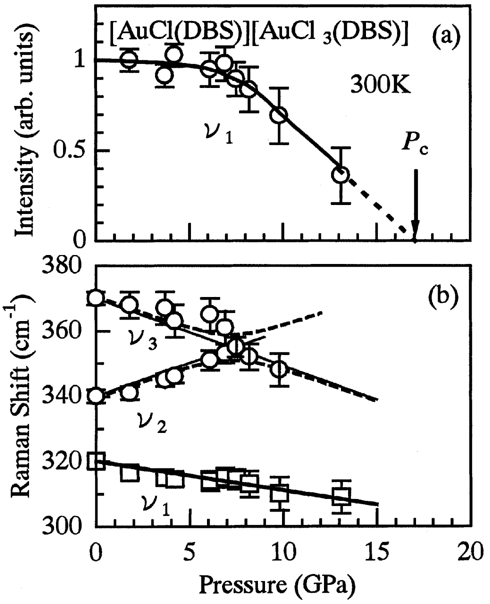

FIGURE 3 Pressure dependence of (a) intensity of the ν_1 mode and (b) frequencies of the ν_1, ν_2 and ν_3 modes of [AuCl(DBS)][AuCl$_3$(DBS)] at 300 K. Broken curves in (b) are the calculated results based on the Fermi resonance model. Solid lines indicate the least-square-fitted results in the case of no mode mixing. P_c shows the critical pressure for the MV-SV phase transition.

renormalized frequencies $\omega_\pm$ are described as:

$$\omega_\pm = \frac{\omega_2 + \omega_3}{2} \pm \sqrt{\frac{(\omega_3 - \omega_2)^2}{4} + C^2},$$

where C is the coupling constant, ω_2 and ω_3 are frequencies of the ν_2 and ν_3 modes, respectively[11]. The coupling constant C is determined to be 4 cm^{-1}, which well reproduces the pressure variation of the mode frequencies, as indicated by broken curves in Figure 3(b). At ambient pressure, the mixing of the modes is small due to the large energy separation (ω_3 -ω_2=30 cm^{-1}), and hence the base frequencies, ω_2 and ω_3 are obtained. A similar pressure-induced Fermi resonance effect was reported in one-dimensional (1D) hydrogen-bonded molecular system, such as cyclopentanedione (CPD) and 3-hydroxydibenzo[a,c]tropone (DBT)[12].

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