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Optical absorption of linear-chain gold complexes under pressure: AuX_2 dibenzylsulfide (X_2=Cl_2,Br_2,ClBr)

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The effect of pressure on the polarized optical absorption spectra of the quasi-one-dimensional (1D) halogen-bridged mixed-valence gold complexes $AuCl_2$(DBS), $AuBr_2$(DBS), and AuClBr(DBS) (with DBS denoting dibenzylsulfide) has been studied up to 6 GPa. The visible absorption edges for light polarized parallel to the chain direction, corresponding to intrachain charge-transfer transitions, exhibit exceptionally large initial red shifts ranging from −0.21 to −0.29 eV/GPa, which is interpreted as a characteristic feature of quasi-1D charge-density-wave systems. The pressure dependence of the visible absorption edges for polarization perpendicular to the chain direction supports an interpretation in terms of interchain charge-transfer transitions. The results for Au complexes are compared with those for the related 1D platinum complexes.

I. INTRODUCTION

A common structural element of quasi-one-dimensional (1D) halogen-bridged mixed-valence metal complexes (HMMC) is a linear chain of alternating metal (M) and halogen (X) ions, which is instable against forming a Peierls-distorted ground state.[1,2] The formal oxidation state of the metal alternates along the chain, and there is a corresponding variation in the metal-halogen bond distance. The charge-density-wave (CDW) ground state in HMMC's results in semiconducting behavior with optical gaps in the visible spectral range. A typical example is Wolffram's red salt (WRS), being one of the well-known Pt-based compounds.[3]

Due to large electron-phonon coupling, the application of external pressure is an effective method for a systematic investigation of the physical properties of 1D HMMC's. In the case of halogen-bridged mixed-valence *platinum* complexes (HMPC's), the pressure dependences of the electrical resistance, optical absorption edges, luminescence spectra, Raman frequencies, and lattice parameters of WRS and some other HMPC's have been investigated.[4–10] A common feature in these materials is that the amplitude of the commensurate CDW is continuously reduced under pressure resulting in strong variations or anomalies in electronic excitations and vibrational properties.

In this paper we report high-pressure optical-absorption spectra of three halogen-bridged mixed-valence *gold* complexes (HMGC's). Only recently, the crystal structure of $AuCl_2$(DBS) [DBS (dibenzylsulfide) is $S(CH_2C_6H_5)_2$] and some optical and vibrational properties of $AuCl_2$(DBS), $AuBr_2$(DBS), and AuClBr(DBS) have been investigated at ambient conditions.[11,12] A schematic representation of the crystal structure of $AuCl_2$(DBS) is shown in Fig. 1. The formal oxidation states of gold are

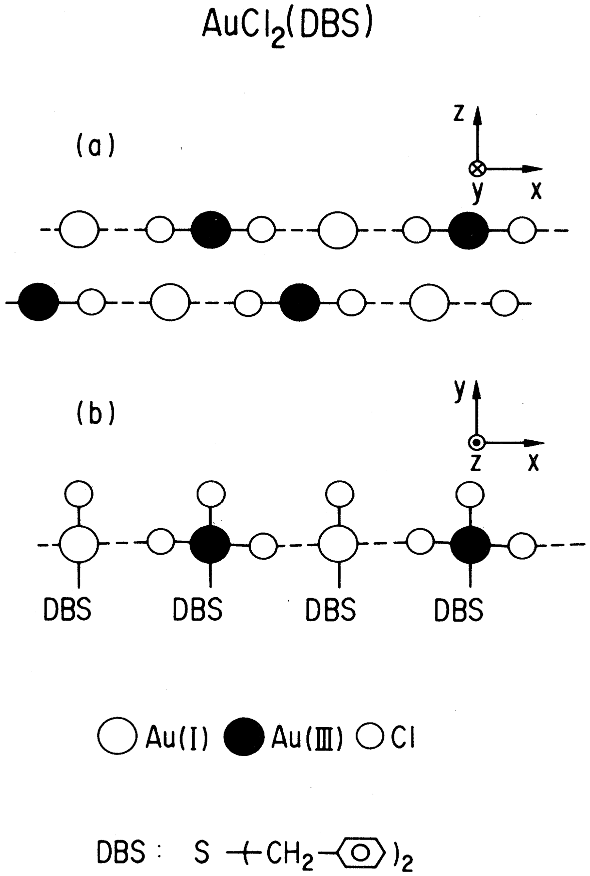

FIG. 1. Schematic representation of the crystal structure of $AuCl_2$(DBS): (a) Relative arrangement of two chains seen from the y direction. (b) A view of one chain from the z direction.

Au(I) and Au(III). The bridging halogens within the chains are positioned closer to the Au(III) ions, thus giving rise to the Peierls-distorted ground state. An important structural difference to the nearly ideal 1D system of many HMPC's is that $AuCl_2(DBS)$ has a paired-chain structure. Both AuClBr(DBS) and $AuBr_2(DBS)$ are suggested to have similar crystal structures.[11,12] In AuClBr(DBS), all bridging halogens (denoted X) are bromines and ligand ions (X') are chlorines.

The optical gaps of the gold complexes for electric field vector **E** polarized parallel to the chain direction **x** ($\mathbf{E}\|\mathbf{x}$) are about 2 eV. In analogy to the optical properties of HMPC's (see, e.g., Ref. 1), these excitations have been interpreted as Au(I)→Au(III) charge-transfer transitions within the chain, i.e., from $d_{x^2-y^2}$ orbitals of Au(I) to $d_{x^2-y^2}$ orbitals of Au(III) by way of the p_x orbitals of the bridging halogen ion.[12,13] The values of the optical gaps are in part determined by the large Peierls distortion and a correspondingly large CDW amplitude. In contrast to Pt complexes, the three gold complexes considered here also show a *visible* optical absorption edge for polarization perpendicular to the chain direction ($\mathbf{E}\perp\mathbf{x}$), at energies 0.2 to 0.5 eV higher compared to $\mathbf{E}\|\mathbf{x}$. This absorption has been interpreted[12] as an *interchain* charge-transfer transition arising from the paired chain structure.

We have measured high-pressure optical absorption spectra of $AuCl_2(DBS)$, $AuBr_2(DBS)$, and AuClBr(DBS) in the range up to 6 GPa at $T=300$ K for $\mathbf{E}\|\mathbf{x}$ and $\mathbf{E}\perp\mathbf{x}$. The primary motivation for the present optical study of HMGC's is that the pressure dependence of the absorption edges in HMGC's provides a test of the proposed assignment of the electronic transitions. Moreover the pressure study is intended to provide information on the resemblance and difference with related Pt complexes and on the general characteristics of 1D CDW states in HMMC's.

II. EXPERIMENTAL DETAILS

The preparation of samples of $AuCl_2(DBS)$, $AuBr_2(DBS)$, and AuCl(DBS) is described elsewhere.[12] The needle-shaped orange crystals obtained after recrystallization were 0.05–0.2 mm thick. Polarized optical absorption spectra were measured by using a diamond window high-pressure cell in combination with a microoptical system.[14] The pressure medium was a one-to-one mixture of pentane and iso-pentane, which provides isotropic pressure conditions up to ~7 GPa. Pressures were determined from the red shift of the ruby R-line luminescence.[15] Diamond windows were selected for low birefringence. Polarizers were used for incident as well as transmitted light. Optical absorption coefficients $\alpha(\omega)$ were determined according to

$$\alpha(\omega)=(1/d)\ln[I_0(\omega)/I(\omega)]\ , \qquad (1)$$

where $I(\omega)$ is the intensity transmitted through the sample at photon energy $\hbar\omega$, and $I_0(\omega)$ is the reference intensity measured through the cell next to the sample. The thickness d of the samples was determined from visual observation under a microscope. Equation (1) neglects sample reflectivity and thus leads to a nonvanishing value of $\alpha(\omega)$ in the region of transparency which is of no significance here.

III. EXPERIMENTAL RESULTS

Figure 2 shows polarized absorption spectra of (a) $AuCl_2(DBS)$, (b) $AuBr_2(DBS)$, and (c) AuClBr(DBS) at different pressures and for polarization $\mathbf{E}\|\mathbf{x}$ and $\mathbf{E}\perp\mathbf{x}$. The absorption edges shift continuously to lower energy under pressure. The absorption edge for $\mathbf{E}\perp\mathbf{x}$ in $AuCl_2(DBS)$ and AuClBr(DBS) broadens slightly with increasing pressure. However, this effect is negligible in the following discussion.[16]

The pressure dependence of the absorption edge energies E_{th} in both polarizations is shown in Fig. 3 for (a) $AuCl_2(DBS)$, (b) $AuBr_2(DBS)$, and (c) AuClBr(DBS) together with those of the reference compounds $Au(III)Cl_3(DBS)$ in (a) and $Au(III)Br_3(DBS)$ in (b). The energies given in Fig. 3 correspond to an absorption

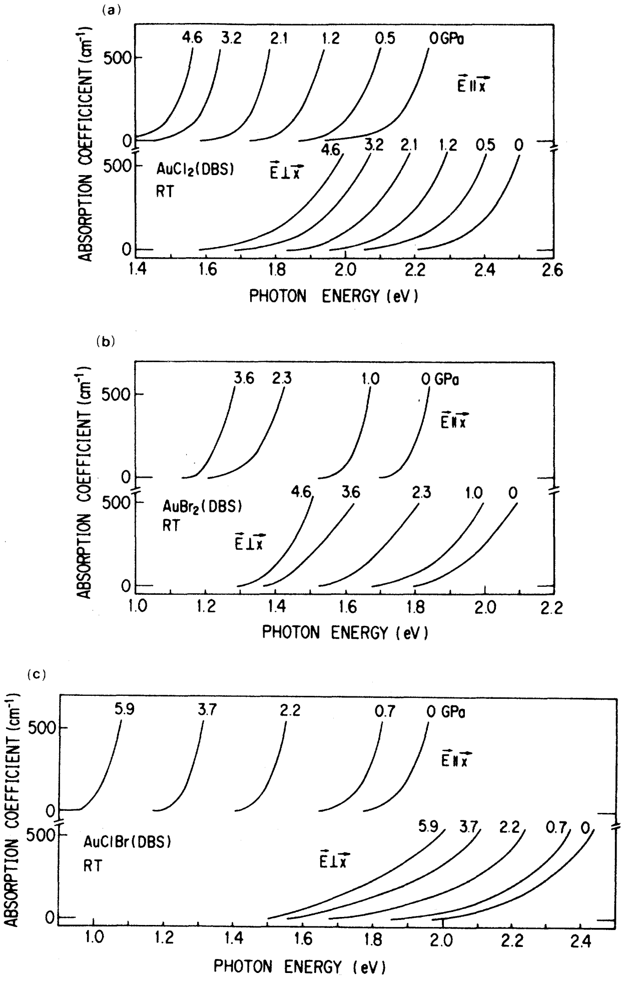

FIG. 2. Polarized absorption spectra of (a) $AuCl_2(DBS)$, (b) $AuBr_2(DBS)$, and (c) AuClBr(DBS) at different pressures.

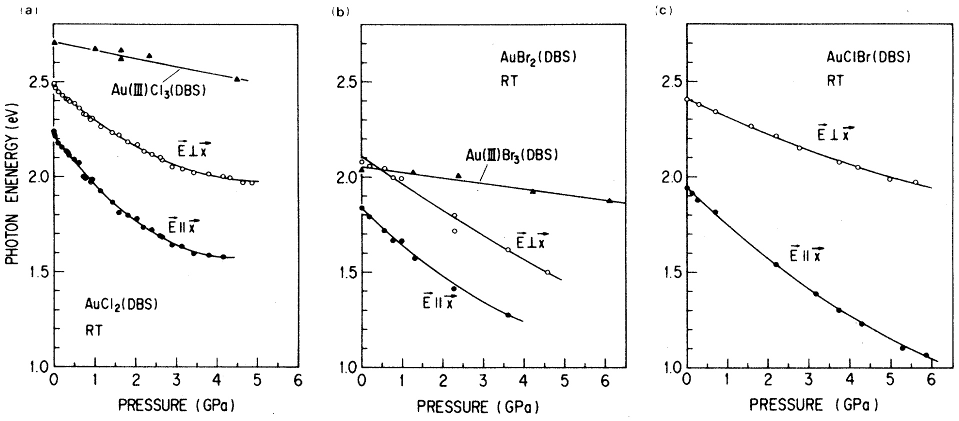

FIG. 3. Polarized absorption-edge energies of (a) $AuCl_2$(DBS), (b) $AuBr_2$(DBS), and (c) AuClBr(DBS) as a function of pressure. Energies refer to an absorption coefficient of $\alpha=500\ cm^{-1}$. Solid lines correspond to the result of a least-squares fit of Eq. (2) to the experimental data. For comparison, some data for Au(III)Cl_3(DBS) in (a) and Au(III)Br_3(DBS) in (b) are also presented.

coefficient $\alpha=500\ cm^{-1}$. The red shift of E_{th} is strongly nonlinear in $AuCl_2$(DBS) for **E**∥**x** as well as **E**⊥**x**. Within the sensitivity of the present experiment we find no evidence for a phase transition in HMGC's up to 5–6 GPa.[17] The solid lines in Fig. 3 correspond to the results of a least-squares fit of a quadratic relation

$$E_{th}=E_0+bP+cP^2 \qquad (2)$$

to the experimental data. The linear and quadratic coefficients b and c are summarized in Table I together with those of the two reference compounds Au(III)Cl_3(DBS) and Au(III)Br_3(DBS) and some related materials.

TABLE I. Absorption edge energies and their linear and quadratic pressure coefficients [see Eq. (2)] of $AuCl_2$(DBS), AuClBr(DBS), and $AuBr_2$(DBS), and related compounds at $T=300$ K. Normalized Peierls distortions δ are also given.

	E_0 (eV)	b (eV/GPa)	c (eV/GPa^2)	δ
$AuCl_2$(DBS)				0.20[a]
E∥**x**	2.22	−0.29	3.3×10^{-2}	
E⊥**x**	2.47	−0.19	1.9×10^{-2}	
AuClBr(DBS)				0.15[a]
E∥**x**	1.94	−0.21	0.9×10^{-2}	
E⊥**x**	2.41	−0.10	0.4×10^{-2}	
$AuBr_2$(DBS)				0.16[a]
E∥**x**	1.83	−0.21	1.5×10^{-2}	
E⊥**x**	2.10	−0.15	0.4×10^{-2}	
Au(III)Cl_3(DBS)				
(unpolarized)	2.70	−0.04		
Au(III)Br_3(DBS)				
(unpolarized)	2.05	−0.03		
WRS[b]				0.16[b]
E∥chain	1.97[c]	−0.7 ($p<0.3$ GPa)[d]		
		−0.2 ($p>0.3$ GPa)		
Pt(en)Cl[e]				0.14[e]
E∥chain	2.17[f]	−0.25[g]		
trans-$(CH)_x$	1.3[h]	−0.15[h]		

[a] Reference 12.

[b] Wolffram's red salt (WRS), [Pt(II)$(EA)_4$][Pt(IV)$Cl_2(EA)_4$]$Cl_4\cdot4H_2O$, where EA (ethylamine) is $C_2H_5NH_2$. See Ref. 18.

[c] Reference 3.

[d] Reference 8.

[e] Pt(en)Cl; [Pt(II)$(en)_2$][Pt(IV)$Cl_2(en)_2$]$(ClO_4)_4$, where en (1,2-diaminoethane) is $NH_2CH_2CH_2NH_2$. See Ref. 19.

[f] Reference 20.

[g] Reference 10.

[h] Reference 21.

For all three HMGC's investigated here, the initial red shift for $\mathbf{E}\|\mathbf{x}$ is larger than for $\mathbf{E}\perp\mathbf{x}$. Figure 4 shows the change with pressure of the polarization-dependent splitting $E_{th}(\mathbf{E}\perp\mathbf{x})-E_{th}(\mathbf{E}\|\mathbf{x})$ of absorption edges. We note from Fig. 4 that the increase of the splitting starts to saturate near 3–4 GPa for $\mathrm{AuCl_2(DBS)}$ and $\mathrm{AuBr_2(DBS)}$, but not for AuClBr(DBS).

The red shift of the absorption edges of the HMGC's in both polarizations is significantly larger compared with that of the two reference compounds $\mathrm{Au(III)Cl_3(DBS)}$ and $\mathrm{Au(III)Br_3(DBS)}$. We emphasize that the initial pressure shifts of the absorption edges for $\mathbf{E}\|\mathbf{x}$ are also exceptionally large compared to those for, e.g., inorganic tetrahedral semiconductors[22] or organic molecular crystals.[23]

IV. DISCUSSION

The 1D chains of HMGC's are surrounded by large organic ligands and are well separated from neighboring chains, except for the chain pairing. Hence, although the three-dimensional coupling will increase under pressure, we expect that the pronounced 1D character of the HMGC's is preserved at the moderate pressures of the present investigation. The following discussion, which is based on this assumption, is mainly qualitative, because results from high pressure x-ray diffraction studies, which could provide detailed information on changes of unit-cell dimensions and the Peierls-like distortion, are not yet available.

We may safely assume that not only the interchain distance but also the lattice parameter along the chain decreases under pressure. At least for HMPC's this behavior has been confirmed experimentally.[9] Thus, we expect a decreasing distance $d_{\mathrm{Au}}=d$[Au(III)-Au(I)] between Au ions along the chain axis. Furthermore, the distance $d_1=d$[Au(III)-X] between Au(III) and bridging halogens X is expected to be less sensitive to pressure because the bonding character is more like that of an intermolecular coordination bond. This picture corresponds to the model of a separated mixed-valence system, i.e., an alternating sequence of Au(I)X(DBS) and Au(III)X_3(DBS) molecules along the chain, which are weakly coupled to each other at ambient pressure. Hence, in the chain direction, it is mainly the distance between Au(I) and X, $d_2=d$[Au(I)-X], which will be shortened under pressure. Thus, the normalized Peierls distortion $\delta=(d_2-d_1)/d_{\mathrm{Au}}$ is expected to decrease. We can also expect a corresponding decrease of the amplitude of the CDW, i.e., of the fractional charge ρ in the notation $-\mathrm{Au}^{2-\rho}-X-\mathrm{Au}^{2+\rho}-X-$. This mechanism results in a decrease of the gap energy, which contributes to the red shift of the absorption edge for $\mathbf{E}\|\mathbf{x}$ under pressure and therefore accounts for the large initial values of the corresponding absorption edge shifts.

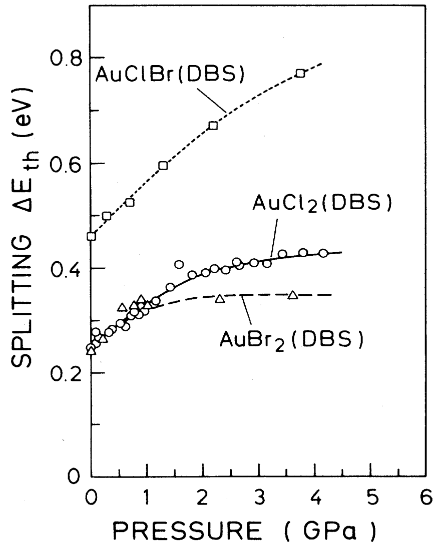

FIG. 4. Splitting ΔE_{th} of the polarized absorption edges of $\mathrm{AuCl_2(DBS)}$, $\mathrm{AuBr_2(DBS)}$, and AuClBr(DBS) as a function of pressure. Lines are guides to the eye.

The value of the initial red shift for $\mathbf{E}\|\mathbf{x}$ in HMGC's appears to be correlated with the magnitude of the Peierls distortion δ at $P=0$. $\mathrm{AuBr_2(DBS)}$ with $\delta=0.16$ and AuClBr(DBS) with $\delta=0.15$ have almost the same value of -0.21 eV/GPa. $\mathrm{AuCl_2(DBS)}$, which has the largest Peierls distortion of $\delta=0.20$ among the HMMC's, shows nearly the largest pressure dependence reported so far, except for the case of WRS.[24]

A relatively large initial red shift of the optical-absorption edge with pressure for $\mathbf{E}\|\mathbf{x}$ is a general aspect of HMMC's, as indicated by the available results for Pt-based compounds given in Table I. Also, transpolyacetylene with a bond ordered wave (BOW) ground state, which is similar to a CDW system,[2,25,26] exhibits a large initial red shift of the absorption edge (see Table I). This apparently general behavior is plausible because the optical gap of a CDW or BOW system is not only affected by the overall compression or change of unit cell dimensions under pressure but also by the change of the normalized Peierls-type distortion, which corresponds to an internal positional parameter of the structural unit cell.

At ambient pressure, $\mathrm{AuCl_2(DBS)}$ has a larger value of δ than Cl-bridged Pt compounds, and similarly for $\mathrm{AuBr_2(DBS)}$ and AuClBr(DBS) in comparison to Br-bridged Pt compounds. The reason for the large δ may be that the interaction between Au(I) and X is weaker than the corresponding interaction in HMPC's, because in $\mathrm{AuX_2(DBS)}$ the $d_{x^2-y^2}$ orbitals are involved instead of the d_{z^2} orbitals in the case of Pt compounds. At present it is not understood whether the large initial shift of the absorption edges is also related to a weaker electron transfer interaction for the $d_{x^2-y^2}$ orbitals of Au ions at ambient pressure.

The red shift of the absorption edge energies for $\mathbf{E}\perp\mathbf{x}$ is significantly larger compared to that of related Au(I) or Au(III) compounds. If the absorptions for $\mathbf{E}\perp\mathbf{x}$ were due to charge-transfer excitations from side ligands X' to Au(III) we would expect pressure coefficients smaller than those for the reference compounds, because the electronic charge on the Au(III) ions is expected to increase with decreasing Peierls distortion. Thus, the relatively large red shift for **E**⊥**x** basically supports the assignment to an interchain charge-transfer transition. This excitation is thought[12] to correspond to a transition from a d_{z^2} orbital of Au(I) to a $d_{x^2-y^2}$ orbital of Au(III) in the neighboring chain by way of the p_z and p_x orbitals of a bridging halogen X. However, one difficulty with this interpretation appears to be that the absolute value of the absorption edge energy for **E**⊥**x** is obviously determined by the side ligand species X'.

The red shift of the absorption edges in HMGC's for **E**‖**x** is sublinear and the decrease of the gap energies slows down at higher pressures. This effect is most pronounced for $AuCl_2$(DBS). The strong nonlinearity may partly be explained within a Peierls-Hubbard–type model;[25] in the higher-pressure regime the Coulomb repulsion energy, which depends on the halogen species, will suppress the further decrease of the optical charge-transfer gap.

The pressure dependence of the splitting of absorption edges for **E**‖**x** and **E**⊥**x** in the three HMGC's, as shown in Fig. 4, indicates that the anisotropic character of the electronic states initially increases under pressure. This simply appears to be a consequence of the reduction of the Peierls distortion. The saturation of the increase in splitting at pressures near 3 to 4 GPa in $AuCl_2$(DBS) and $AuBr_2$(DBS) seems to mark the point where Coulomb repulsion becomes more important for the pressure dependence of the Au(I)→Au(III) charge-transfer excitation energies.

V. CONCLUSIONS

We summarize the results of the present high-pressure optical absorption study of the linear-chain gold complexes $AuCl_2$(DBS), $AuBr_2$(DBS), and AuClBr(DBS) as follows: (1) The energies of the optical absorption edges of HMGC's exhibit a strong initial red shift with increasing pressure for **E**‖**x**. This effect is attributed to a reduction of the Peierls distortion and appears to be a characteristic feature of 1D semiconductiong CDW systems. (2) The initial pressure coefficients of absorption edges for **E**‖**x** in HMGC's scale to some extent with the normalized Peierls distortion δ at ambient pressure. (3) The absorption edges for **E**⊥**x** exhibit a larger red shift with increasing pressure compared to that for the trivalent reference compounds Au(III)Cl_3(DBS) and Au(III)Br_3(DBS). This result supports an assignment of these absorption edges to *interchain* charge transfer excitations between paired chains. (4) Coulomb repulsion starts to contribute to the pressure dependence of absorption edges for **E**‖**x** at pressures near 3 to 4 GPa, as indicated by the strong sublinearity of the red shift in $AuCl_2$(DBS) and the saturation effect of the polarization-dependent splitting in $AuCl_2$(DBS) and $AuBr_2$(DBS).

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