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Reflection and Absorption Edge Spectra in Mercurous Halide Single Crystals

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The reflection and absorption edge spectra in Hg_2I_2 and Hg_2Br_2 single crystals were measured in the visible and near ultraviolet region at various temperatures. The exciton transition of the lowest energy was assigned as the direct transition for $E//c$ between the bonding and antibonding states of the Hg–Hg bond. The high temperature steepness constant was obtained to be 0.53 in Hg_2I_2 from the analysis of the absorption edge, suggesting the strong exciton—LO phonon interaction in this crystal.

§1. Introduction

Mercurous halides Hg_2X_2 (X=Cl, Br, I) are molecular crystals with symmetry D_{4h}^{17} consisting of parallel chains of a linear molecule X–Hg–Hg–X. The bond between adjacent molecules is of van der Waals type, while the intramolecular bonding is mainly covalent. The crystal structure leads to an extremely strong optical and elastic anisotropies. For example, Hg_2Cl_2 has a high optical birefringence ($n_{//}-n_{\perp}=0.65$ at ~ 2 eV)[1] and very low sound velocity[2] for basal plane shear wave along [110]. So far, their lattice vibration and structural phase transition have been extensively investigated through the measurements of Raman scattering or infrared absorption.[3-5]

Concerning the electronic transitions, the absorption measurements were done for Hg_2I_2 single crystals by Turyanitsa *et al.*[6] and for thin films of mercurous halides by Deb.[7] On the thin films, several absorption peaks were observed; some of them were assigned to a hydrogenic series of their exciton states. However, as far as the reflection spectrum of the single crystal is concerned, there is only one brief report about Hg_2Cl_2 single crystals at room temperature,[8] which indicates a strong anisotropy: only for the incident light with its electric vector E parallel to the c-axis of the crystal, a large structure-less peak has been observed at 34.8 kcm^{-1}.

In the present paper, we report the reflection and absorption associated with the electronic transition of Hg_2I_2 and Hg_2Br_2 single crystals in the visible and near ultraviolet region for the temperature range of 4.2 K to 270 K and discuss the origin of the structures in the reflectivity spectra and the exciton-lattice interaction.

§2. Experimentals

We sealed 5N red—HgI_2 powder obtained from Aldrich Chemical Company and a stoichiometric excess of 6N mercury metal in a glass ampoule with the diameter of 14 mm and the length of 100 mm under vacuum. Then the ampoule was put into a horizontal furnace and the HgI_2 source at the edge of the ampoule was kept at 160°C. After 70 hours, we obtained some rectangular shaped Hg_2I_2 single crystals with the dimension of a few mm at the other edge of the ampoule where the temperature was a few degree below the source temperature. The used Hg_2Br_2 single crystals were grown by a similar method in which the source temperature was 300°C. The mostly well-developed surfaces of Hg_2I_2 and Hg_2Br_2 crystals were identified to be parallel to the c-axis by the X-ray diffraction pattern. The samples were sealed in quartz tubes filled with He gas and were kept at 260 K to avoid the dissociation into HgX_2 and Hg.

For the reflection and absorption measurements, deuterium and candescent lamps were

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used as a light source, respectively. The light from the lamp was focussed on the surface of the crystal immersed in liquid He or kept at a given temperature between 4.2 K and 270 K within the temperature variation of ± 2 K by using the temperature control system. The reflected or transmitted light was passed through a linear polarizer and focussed onto the entrance slit of a Jobin-Yvon U-1000 double monochromator. The output current of the photomultiplier was measured by the DC-method. The absolute reflectivity was calculated with using the refractive index in the transparent wavelength region estimated from the measurement of the Brewster angle. The absorption coefficient has been corrected for the reflection loss estimated from the measured reflectivity.

§3. Experimental Results

Solid curves of Fig. 1 show the reflection spectra of Hg_2I_2 at 4.2 K for the lights polarized parallel and perpendicular to the c-axis. In the $E//c$ spectrum, there are two groups of structures near 26 kcm^{-1} and 34 kcm^{-1}. In the 26 kcm^{-1} group two sharp peaks are observed at 24.2 kcm^{-1} and 27.2 kcm^{-1}, and the 34 kcm^{-1} group includes three peaks at 32.0 kcm^{-1}, 33.6 kcm^{-1} and 35.1 kcm^{-1}. On the contrary, there is no dominant peak in the $E\perp c$ spectrum. Dash-dotted and broken curves show the $E//c$ spectra at 77 K and 200 K, respectively. The two peak energies of the 26 kcm^{-1} group shift to the lower energy side by $\sim$0.5 kcm^{-1} with the change in temperature from 4.2 K to 200 K.

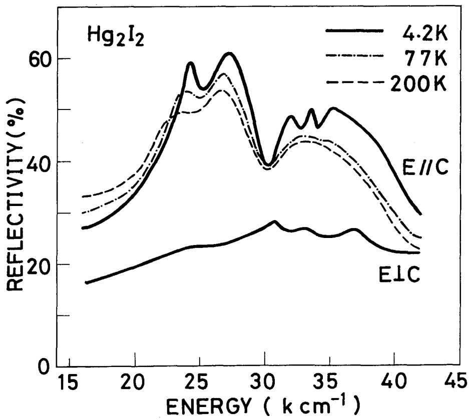

Fig. 1. Reflection spectra of Hg_2I_2 for $E//c$ and $E\perp c$ polarizations at 4.2 K (solid curves) and for $E//c$ at 77 K (dash-dotted curve) and 200 K (broken curve).

In Fig. 2 are shown the reflection spectra of Hg_2Br_2 at 200 K. The spectra at the lower temperatures were not measured because the structural phase transition occured at 143 K.[9] In the $E//c$ spectrum two peaks are located at 31.0 kcm^{-1} and 34.0 kcm^{-1}, respectively, which perhaps correspond to the 24.2 kcm^{-1} and 27.2 kcm^{-1} peaks of Hg_2I_2. The structure associated with the higher energy group is not observed, probably because of its too high energy beyond our measurable spectral range. On the other hand, in the $E\perp c$ spectrum there appears no dominant structure as in the case of Hg_2I_2.

The fundamental absorption tails of Hg_2I_2 were measured at various temperatures between 4.2 K and 270 K. The measurement was mainly performed for $E\perp c$, since the crystals had wedged shape and the precise measurement for $E//c$ was not successful on account of the considerably large dispersion. The absorption coefficient for $E\perp c$, as shown in Fig. 3, is represented in the logarithmic scale where the reflection loss has been corrected. The open circles indicate the experimental points. The solid lines represent the following Urbach's formula:[10]

$$\alpha=\alpha_0 \exp\left(-\sigma\frac{h\nu_0-h\nu}{k_B T}\right), \qquad (1)$$

where α is the absorption coefficient, $h\nu$ the photon energy, k_B the Boltzmann constant and T the absolute temperature. Here, we use the adjustable parameters $\alpha_0 \simeq 1\times10^7$ cm^{-1} $h\nu_0 \simeq$ 24 kcm^{-1} and the temperature dependent

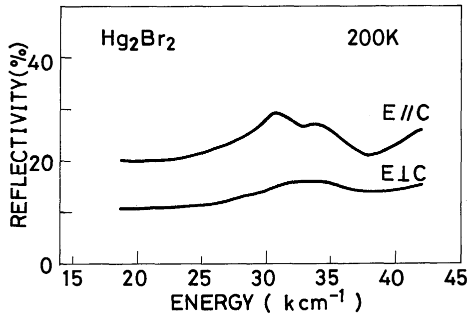

Fig. 2. Reflection spectra of Hg_2Br_2 at 200 K for $E//c$ and $E\perp c$ polarizations.

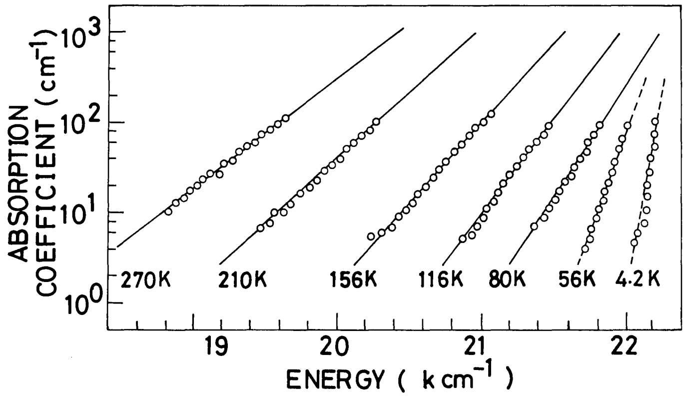

Fig. 3. Temperature dependence of the absorption coefficient at the fundamental absorption edge of Hg_2I_2 for the $E \perp c$ polarization (open circles). Solid lines represent eq. (1) of the text with $\alpha_0 \simeq 1 \times 10^7$ cm^{-1} and $h\nu_0 \simeq 24$ kcm^{-1}.

steepness constant σ. The experimental points at the temperatures higher than 80 K are in good agreement with the Urbach's formula. The experimental values at 4.2 K and 56 K, however, are not represented by the same formula. This disagreement seems to originate from the defects or impurities in the crystal.[11]

The experimental steepness constants σ at various temperatures are shown by open circles in Fig. 4. The solid curve shows the calculated steepness constant expressed by

$$\sigma = \sigma_0 \frac{2k_B T}{\hbar\omega} \tanh \frac{\hbar\omega}{2k_B T}, \quad (2)$$

with the adjustable parameters $\sigma_0 = 0.53$ and $\hbar\omega = 138$ cm^{-1}. We obtain the best fit with the experimental points in the temperature range from 80 K to 270 K.

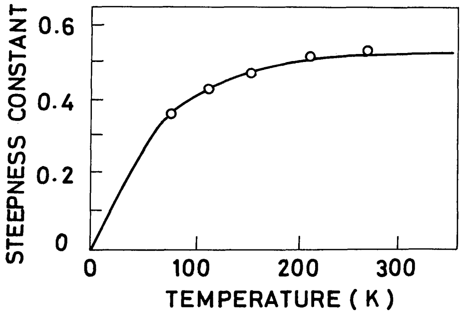

Fig. 4. Open circles show the temperature dependence of the steepness constant σ estimated from the straight line in Fig. 3. A solid curve represents eq. (2) of the text with the ajustable parameters $\sigma_0 = 0.53$ and $\hbar\omega = 138$ cm^{-1}.

§4. Discussion

As the mercurous halide crystals are of molecular type, the structures due to the electronic transitions in a Hg_2X_2 molecule are expected to appear in the reflection spectrum of the crystal. According to the molecular orbital calculation of a Hg_2Cl_2 linear molecule by Kleier and Wadt,[12] the dipole allowed transition from the bonding $^1\Sigma_g^+$ to antibonding $^1\Sigma_u^+$ states mainly constracted from the two 6s-orbitals of mercury is expected to occur as the lowest energy transition. This transition is allowed for the light with the electric vector parallel to the molecular axis, resulting that it is allowed for $E // c$ in the crystal. The above suggestion is consistent with the experimental results of Figs. 1 and 2. In practice, the transition becomes partially allowed even for $E \perp c$ as shown in Fig. 3.

The electronic transition between the bonding and antibonding states of the two metallic orbitals is also observed in the absorption spectrum of a layer semiconductor GaSe in which the band structure has been calculated by Schlüter.[13] According to his calculation, the band gap decreases abruptly as the distance between the two metal atoms increases. The validity of this relation has been checked for mercurous halides as shown in Table I. The second column of Table I represents the two peak energies of the lower energy group of the reflection spectra in Hg_2I_2 and Hg_2Br_2, and the peak energy of the absorption band in

Table I. The second column represents the peak energies of the lower energy group in Hg_2I_2 and Hg_2Br_2, and the energy of the absorption band in Hg_2Cl_2 reported by Perekalina *et al.*[8] The third column shows the distance between the two mercury atoms in the crystal.

	peak energy (kcm^{-1})			Hg–Hg
Hg_2I_2	23.7	26.7	(200 K)	2.69 Å
Hg_2Br_2	31.0	34.0	(200 K)	2.58 Å
Hg_2Cl_2	34.8		(300 K)	2.53 Å

Hg_2Cl_2 reported by Perekalina *et al.*[8] In Hg_2Cl_2, the two peaks are not separated, probably because of the too high temperature. In the last column, the distance of the two mercury atoms is listed. The energy of the lowest peak decreases in order of Hg_2Cl_2, Hg_2Br_2 and Hg_2I_2, while the distance between the two mercury atoms increases. This result qualitatively agrees with his estimation.

The lowest energy reflection peak of Hg_2I_2 is observed at 24.0 kcm^{-1} at 77 K which is 4.4 kcm^{-1} higher than the lowest energy absorption peak in the evaporated film observed by Deb.[7] He has assigned this band to be associated with the 1s exciton formation. However, this absorption band might be associated with the exciton in the mixed crystal of Hg_2I_2 and HgI_2, because its energy is located between the lowest energy peak in the reflection spectrum of the Hg_2I_2 single crystal and the exciton energy of a HgI_2 crystal, 18.7 kcm^{-1}.[14] The first doublet structure in Hg_2I_2 and Hg_2Br_2 and the second triplet structure in Hg_2I_2 may be caused by the hybridization among the s- and d-orbitals of mercury, the p-orbitals of the two nearest halogens and the p-orbitals of the eight next nearest halogens, and/or by the joint density of states. This problem will be solved by the band structure calculation.

The lower energy tail of the absorption band in Hg_2I_2 decreases exponentially and the so-called Urbach rule stands for this energy region. The estimated value of $h\nu_0$, $\sim$24 kcm^{-1}, is close to that of the lowest energy sharp peak in the reflection spectra at 4.2 K in Fig. 1, which may correspond to the exciton formation energy. The amount of the high temperature steepness constant of $\sigma_0=0.53$ estimated from Fig. 4 is close to those of ionic crystals rather than those of semiconductors.[15] The small value of σ_0 indicates a strong exciton-phonon coupling. The estimated average phonon energy of $\hbar\omega=138\ cm^{-1}$ is located near the energy of the A_{2u} longitudinal optical phonon, 150 cm^{-1}.[5] This fact suggests that the electro-static interaction is dominant between the electron (hole) and the phonon in the Hg_2I_2 crystal.

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