Observation of the Simultaneous Amplification of the Space Charge and the Fast Cyclotron Waves in a Spiral Beam-Plasma System

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Fundamental Optical Transitions in the Single Crystal of Cadmium Iodide

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The fundamental reflectivity spectrum of the cleaved surface was measured at room and liquid heliun temperatures in the region 3-12 eV for CdI_2 single crystal. The polarized reflectivity spectra of the polished surface perpendicular to the easy-cleavage face were also measured at liquid nitrogen temperature in the region 3-7 eV.

In the ε_2 spectrum of the cleaved surface analyzed through the Kramers-Kronig procedure, three very sharp exciton lines with half-widths 20-30 meV are embedded in the deep interband scattering continuum. The low energy parts of the spectral behaviors are interpreted in terms of dichroic optical transitions occuring at high symmetry critical points in the Brillouin zone. The upper valence bands are of predominant iodine *p*-like character with a possibility of a certain admixture of cadmium *d*-like wave functions.

1. Introduction

Cadmium iodide crystallizes in a typical layer structure with highly ionic properties. Basic unit of the layer consists of one cadmium-ion-sheet and two iodine-ion-sheets; the cadmium-ion-sheet is sandwiched by the two iodine-ion-sheets. The CdI_2 crystal belongs to the D_{3d}^3 space group with one molecule per unit cell, and has easy-cleavage face parallel to the layer.

Since the cadmium iodide is highly anisotropic, an evaporated film is inadequate for studying its fundamental optical spectra. Optical reflectance spectra of the cadmium iodide single crystal were reported

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by Greenaway and Nitsche[1] (1965), and Greenaway and Harbeke[2] (1966). They measured the spectra of the cleaved surface at liquid nitrogen temperature in the photon energy region of 5.0 - 7.5 eV and found two very sharp lines at deep interband energy region more than 2 eV above the optical gap. Wright and Tubbs[3] (1970) ascribed these two sharp lines to exciton formations on the basis of their measurements on the photoconductivity spectrum.

In the present work the reflectance spectra of the cleaved surface of the cadmium iodide single crystal are measured at room and liquid helium temperatures in the photon energy region of 3-12 eV. From these spectrum, important optical constants are determined through the Kramers-Kronig analysis. The reflectance spectra of the crystal surface polished perpendicularly to the layer are also measured at liquid nitrogen temperature in the region 3-7 eV by using linearly polarized light.

2. Experimental

The reflectance spectra of nearly normal incidence (~ 5°) were measured for cleaved surface perpendicular to the crystllographic c axis and for polished surface parallel to the c axis of the CdI_2 single crystal. The measurements for the cleaved surface were carried out at room temperature (RT) and liquid helium temperature (LHeT) in the photon energy region of 3-12 eV by using a hydrogen discharge tube as a light source. The measurements for the polished surface were carried out at liquid nitrogen temperature (LNT) by using a 200W deuterium lamp as a light source; the light from the source was linearly polarized by a Rochon polarizer placed in front of th light source. All the measurements were carried out by means of a double beam method with the use of a Seya-Namioka vacuum ultraviolet monochromator. Details of the double detection system are reported in ref.4.

Single crystals of CdI_2 were grown from the melt by the Stockbarger technique. The sample surface parallel to the c axis was polished with carborundum of #8000 and was etched by using ethyl-alcohl.

3. Results

Figure 1 shows the reflectivity spectra of normal incidence of the freshly cleaved surface measured at LHeT (solid line) and RT (broken line) in the region 2-12 eV. The reflectivities at photon energies near the absorption edge (3.6 eV at LHeT and 3.4 eV at RT) agree well with those determined from the values of the refractive index $n^{5)}$ by using the relation $R = (n-1)^2/(n+1)^2$. In the transparent region, correction is made for the spectra by subtracting the additional reflection from the back surface of the sample and only the contribution

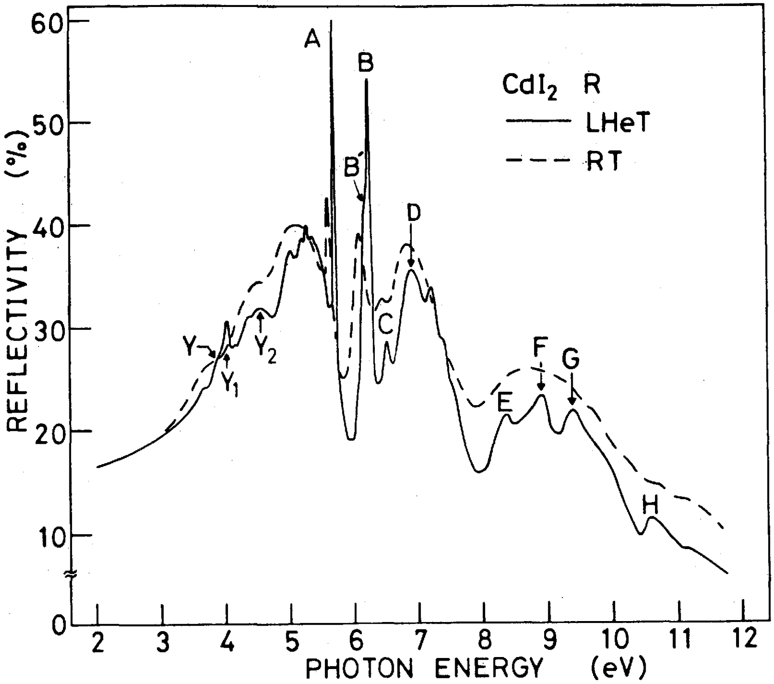

Fig.1. Normal incidence optical reflectivity spectra of the freshly cleaved surface of CdI_2 single crystal measured at liquid helium temperature (solid line) and room temperature (broken line).

from the front surface is shown in the figure. The LHeT spectrum shows well resolved structures in comparison with the reflectivity spectra reported in refs.1-2, which were measured at LNT in the region 4.7-7.6 eV. Several structures are also observed in the lower energy than 4.7 eV.

The real and imaginary parts of the complex refractive index $\hat{n} = n - ik$, which are suitable for the description of optical properties of the medium, are determined with the application of the Kramers-Kronig relation to the R spectra of Fig.1. In the analysis, the reflectivity R supplemented in the lower energy region ($\omega < 2$eV) is assumed to have no reststrahlen band and is approximated by $R(\omega) = R(2\text{eV})$. Above 12 eV, the curve R is extrapolated in the form $R(\omega) = R(12\text{eV}) \times (12/\omega)^p$, where the exponent p is so adjusted that the extinction coefficient k

is zero at 3.6 eV at LHeT and 3.4 eV at RT. (The values of p were 1.125 and 2.174 for the LHeT and RT spectra respectively.) The quantity ε_2 the absorptive or imaginary part of the complex dielectric function, which is an important quantity in studying the optical properties of solids from theoretical point of view, is also computed using the relation $\varepsilon_2 = 2nk$.

The spectra of the optical constants n, k and ε_2 obtained in this way are shown in Figs.2-3. The LHeT spectrum of ε_2 shows well resolved structures compared to that of R of Fig.1. In particular, the

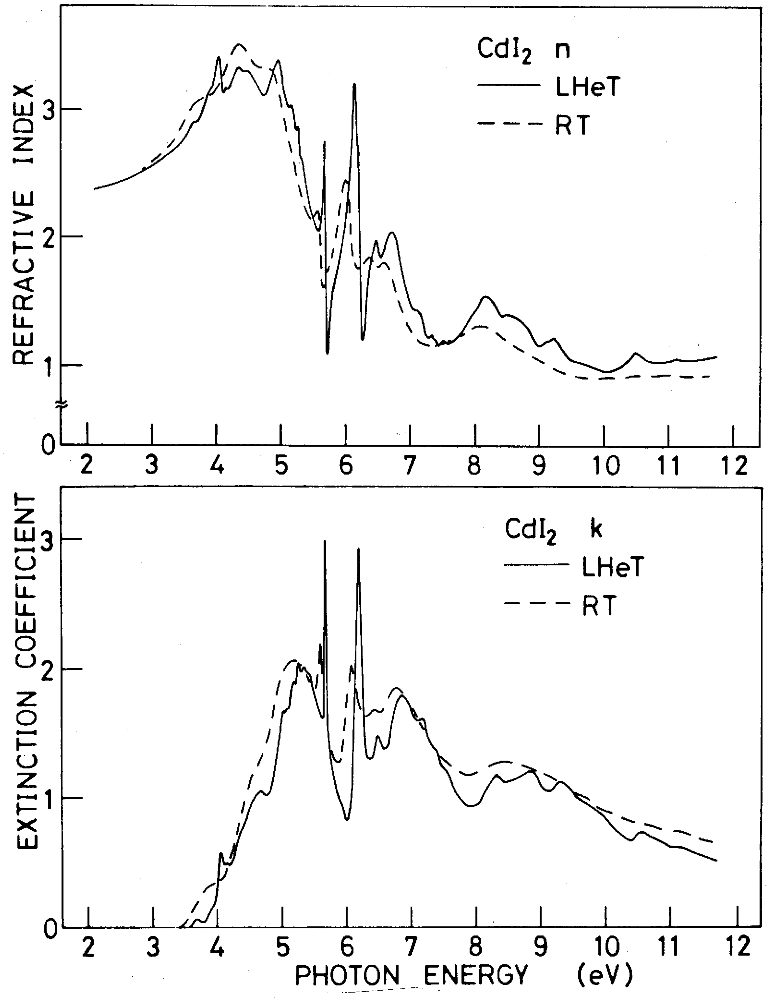

Fig.2. The real and imaginary parts of the complex refractive index $\hat{n} = n - ik$ of CdI_2 for ordinary ray determined from the reflectivity spectra of Fig.1 through the Kramers-Kronig procedure.

structures Y_1 and Y_2 observed in the low energy part appear as clear peaks in the ε_2 spectrum. The two characteristic sharp lines A and B observed in the deep interband energy region sharpen further in the ε_2 spectrum with the half-widths of about 20 and 50 meV respectively. Furthermore the additional structure B' of the low energy part of the line B is more prominent in the ε_2 spectrum than in the R spectrum. It is also noted that the ε_2 spectrum reveals satellite peaks just above the line A. The energy positions of the main structures marked with the letters in Figs.1 and Fig.3 are summarized in Table I.

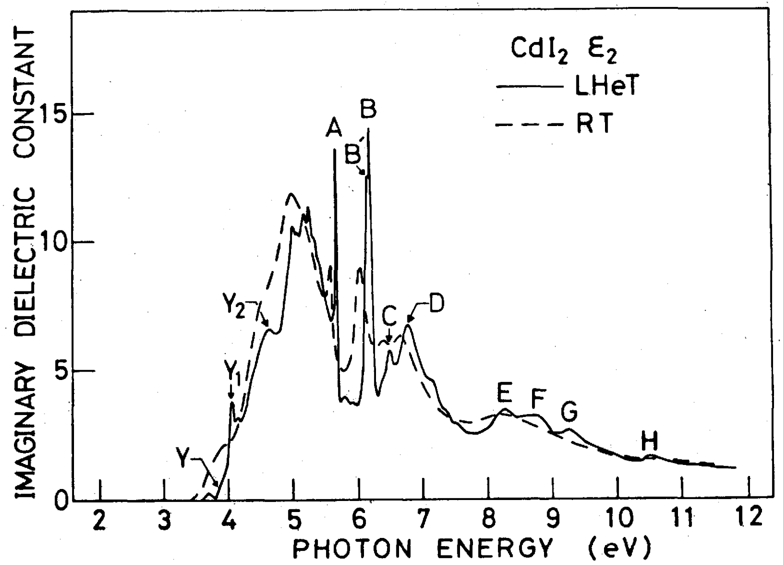

Fig.3. The absorptive or imaginary part of the complex dielectric function of CdI_2 for ordinary ray determined from the reflectivity spectra of Fig.1 through the Kramers-Kronig procedure.

Table I. The energy positions of the main structures observed at liquid helium temperature in the reflectivity spectrum and the ε_2 spectrum of CdI_2 shown in Fig.1 and Fig.3 respectively.

(in eV)

Structure	Y	Y_1	Y_2	A	B'	B
R	3.8	4.035	4.58	5.693	6.15	6.224
ε_2	3.90	4.070	4.64	5.677	6.166	6.200

Structure	C	D	E	F	G	H
R	6.505	6.90	8.34	8.90	9.38	10.58
ε_2	6.480	6.78	8.26	8.80	9.28	10.5

Figure 4 shows the $E\perp c$ and $E\parallel c$ reflectance spectra measured at LNT of the polished surface perpendicular to the easy-cleavage face of CdI_2. The curve $R_\perp$(polished) is the reflectivity spectrum for $E\perp c$ and the curve $R_\parallel$(polished) for $E\parallel c$. For comparison is also shown the reflectivity spectrum of the cleaved surface $R_\perp$(cleaved) measured at the same temperature, which shows the same outline as that reported in refs.1-2 in the duplicated energy region. The spectra of the polished surface were so adjusted that the value of $R_\perp$(polished) coincides with that of $R_\perp$(cleaved) at the absorption edge (3.6 eV). The ratios of the measured reflectivities for $E\parallel c$ to those for $E\perp c$ agree well with the corresponding ones determined from the dichroic refractive index

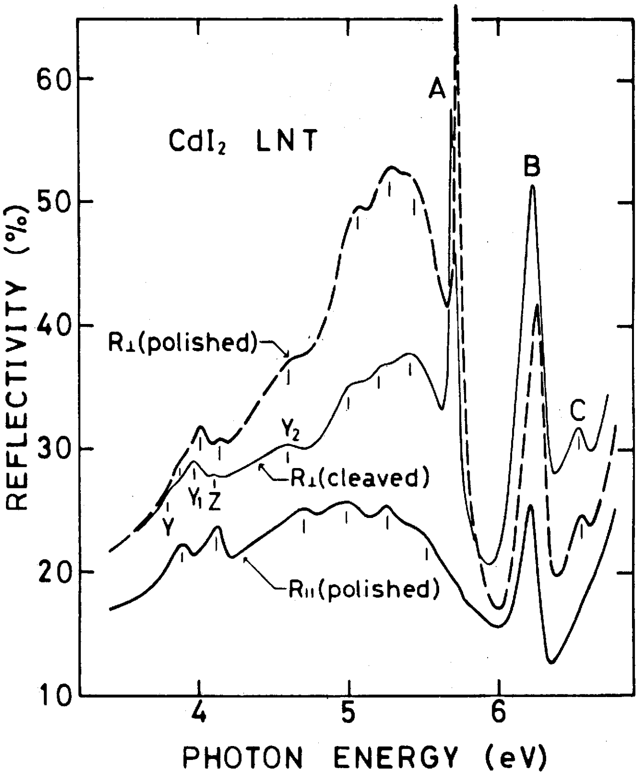

Fig.4. Normal incidence optical reflectivity spectra of the polished surface of CdI_2 perpendicular to the crystallographic c axis measured at liquid nitrogen temperature by using linearly polarized light with the electric vector E perpendicular or parallel to the c axis: $R_\perp$(polished) for $E\perp c$ and $R_\parallel$(polished) for $E\parallel c$. The reflectivity spectrum of the cleaved surface $R_\perp$(cleaved) measured at the same temperature is also shown for comparison.

data[5)] in the transparent region. No missing and no extra structure is observed in the curve R⊥(polished) as compared with the curve R⊥ (cleaved) and the correspondence of the spectral structures between the two curves is fairly good. The slight discrepancy of the energy positions of the spectral structures between the two curves, and the relatively large variation of the $R_\perp$(polished) minus $R_\perp$(cleaved) against the photon energy are due to the difference in quality between the reflecting surfaces (cleaved and polished).

The spectral structures observed for the curve $R_\parallel$(polished) are largely different from those observed for the curve R⊥(polished). In the curve $R_\parallel$(polished) are observed two prominent peaks at the photon energies of 3.88 and 4.11 eV., where the optical transitions for $E \perp c$ are very week (see structures Y and Z). On the other hand, no structure is observed for the curve $R_\parallel$(polished) at 4.00 eV where the strong $E \perp c$ transition responsible for the structure Y_1 occurs. In the higher energy region up to about 5.6 eV, the structures due to interband transitions are about equally visible in both polarizations. However the structures for $E \perp c$ lie on the intense continuum. Above 5.6 eV, noticeable difference are observed between the two curves. No structure is found for the curve $R_\parallel$(polished) at 5.7 eV where the characteristic sharp line A is observed for $E \perp c$. This is contrary to the measurements by Greenaway and Harbeke,[2)] though they did not show the figure of the spectrum for $E \parallel c$ in their paper. The optical transitions around 6.2 eV are commonly observed for both polarizations. It is noted however that the reflectivity maximum for $E \parallel c$ is located at slightly lower energy than that for $E \perp c$. The energy difference between the two maxima is about 40 meV and is comparable to that between the structures B and B' (34 meV) observed at LHeT (Fig.3). No structure is again observed for $E \parallel c$ around 6.5 eV where the structure C appears as a small peak for $E \perp c$.

4. Discussion

Since no electron energy band calculation is available for CdI_2, it is difficult to fully interprete the data of the preceding section in terms of allowed optical interband transitions ocuring at particular critical points in the Brillouin zone. However, some important features of the fundamental spectral behaviors can be explained after a zero order band scheme.

In a zero order band model, the upper valence bands of CdI_2 would be constructed mainly from iodine *5p*-state wave functions, while the lowest conduction band would have its main origin in the cadmium *5s*-state wave function. The origin of the low lying spectral structures of CdI_2 are therefore of predominant character of the allowed interband optical transitions from the iodine *p*-like valence bands to the cationic *s*-like conduction band. In analogy with the cases of the other layer cadmium halides $CdCl_2$ and $CdBr_2$, $^{6-8)}$ it is plausible to assume that the two structures Y_1 and Y_2 shown in Fig.3 come from the spin-orbit interaction of the iodine *p*-like valence band at a high symmetry critical point in the Brillouin zone and the additional structure Y from the critical field perturbation at the same critical point. This assumption is effective to understand the anisotropic behavior of the low energy part of the reflectance spectra shown in Fig.4 as is discussed in the following paragraph.

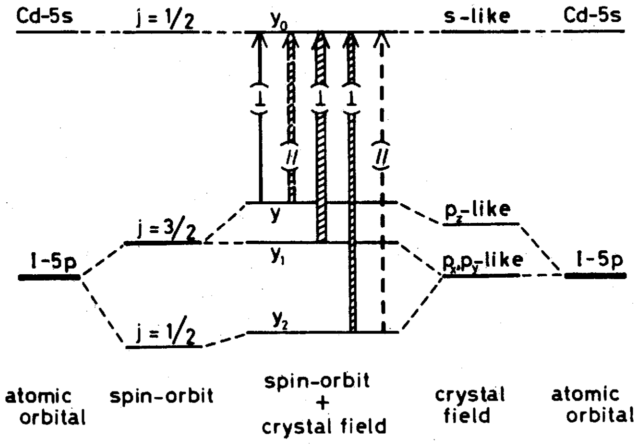

Fig.5. The schematic diagram of the allowed direct optical transitions from the iodine *5p*-like valence bands (y, y_1 and y_2) to the cadmium *5s*-like conduction band (y_0) at high symmetry critical points of the Brillouin zone of CdI_2, i.e., the Γ (D_{3d}), *A* (D_{3d}), *K* (D_3), *H* (D_3) and Δ (C_{3v}) points.

In Fig.5 is shown the schematic diagram of the allowed direct optical transitions from the iodine *p*-like valence bands (y, y_1 and y_2) to the cadmium *s*-like conduction band (y_0) at high symmetry critical points of the Brillouin zone containing in their symmetry groups the operation of the three-fold rotation, that is, the Γ (D_{3d}), A (D_{3d}), K (D_3), H (D_3) and Δ (C_{3v}) points. (At the Γ and A points only the valence bands having the odd-parity wave functions are taken into account, since the cadmium *s*-like conduction state is of even-parity at these critical points.) The wave functions of the valence band y have a predominant p_z-like character with a small admixture of p_x- and p_y-like wave functions due to the spin-orbit interaction. The direct interband optical transition from the valence band y to the conduction band y_0 ($y \rightarrow y_0$) is more active for $E /\!/ c$ than for $E \perp c$ and is therefore believed to gives rise to the strongly anisotropic behavior of the 3.88 eV absorption band shown in Fig.4. Inversely, the wave functions for y_2 have predominant p_x- and p_y-like characters with a certain admixture of the p_z-like wave function; the optical transition $y_2 \rightarrow y_0$ has a large probability for $E \perp c$ compared with that for $E /\!/ c$; this seems to correspond to the anisotropic character of the 4.6 eV band. On the other hand the optical transition $y_1 \rightarrow y_0$ is active only for $E \perp c$ since no hybridization between the p_x- and p_y-like and the p_z-like wave functions occurs in the valence wave functions for y_1 even if the spin-orbit interaction is taken into account. This accounts for the two dimensional character of the electric dipole transition observed at 4.00 eV in Fig.4. As to the 4.11 eV band, no good explanation for the strong anisotropic behavior is found at present.

The energy differences between these iodine p-like valence bands can be estimated by a simple calculation. If the contribution from the other constituent atomic orbitals of CdI_2 such as cadmium $4d$-orbitals to these valence bands are ignored, the energy difference between the valence bands y and y_2, i.e., $\omega(y) - \omega(y_2)$, is easily shown to be more than $\sqrt{8/9}\,\lambda = 0.889$ eV by using eq.(2) of ref.8, where $\lambda = 0.942$ eV is the atomic spin-orbit splitting energy of the iodine p-electron. (We note that, though the quantity $\sqrt{8/9}\,\lambda$ is accidentally equal in magnitude to the well-known minimum splitting of Knox and Inchauspè,9) it is,of course, different in its character from the latter.) The energy difference between the valence bands y_1 and y_2 ,i.e., $\omega(y_1) - \omega(y_2)$, which is equal to λ for zero crystal field, decreases with increasing crystal field and converges to $(2/3)\,\lambda = 0.628$ eV for infinite crystal field. On the other hand the observed energy differences are 0.74 eV for $\omega(y) - \omega(y_2)$ and 0.57 eV for $\omega(y_1) - \omega(y_2)$. Both of these values are somewhat smaller even than the corresponding minima predicted theoretically. These discrepancies suggest a possibility of a certain admixture of the cadmium d-electrons to the upper valence bands due to their relatively shallow atomic energy levels. In fact, such admixture is known to reduce the spin-orbit splittings of the halogen p-like valence bands in the cases of the silver and cuprous halides,10-11) whose constituent atoms have isoelectronic configurations to those of the cadmium halides. It is also noted that the cadmium iodide shows some covalent properties in the dispersion behaviors of the refractive indices5) in favor of the possibility of this type of admixture. It is therefore plausible to relate the three transitions discussed above to one of high symmetry critical poins other than Γ and A points. (At Γ and A points the *p-d* mixing is parity-forbidden owing to inversion symmetry.)

The two characteristic sharp lines A and B (and the structure B') observed in the ε_2 spectrum at LHeT (Fig.3) suggest strong exciton effects in spite of their peak energies more than 2 eV above the optical gap. The peak energies agree well with the dip energies of the photoconductivity spectrum.3) The two satllite peaks observed just above the line A suggest a possible evidence for the second and third members of the well-known Wannier exciton series. However, the peak energies of the satllites (5.797 eV, 5.926 eV) do not satisfy the three dimensional hydrogen model, and the intensity ratio of the first satellite to the line A is very small compared with the 1/8 predicted from the model. The small peak C and the weak shoulder observed just below this peak C might be explained as the second components of the exciton lines B and B' respectively.

As to the 5.7 eV exciton, the associated critical point should be located at the high symmetry critical point in the Brillouin zone since its optical transition vanishs completely for $E \parallel c$ as is shown in Fig.4. In fact, group theoretical arguments show that at any critical point with lower symmtry properties than the Γ, A, K, H and Δ points, no 'completely anisotropic' interband optical coupling is allowed due to star degeneracies. (Of course, no 'completely isotropic' interband optical coupling is also allowed.) Therefore the symmetry properties of the optical transition responsible for the exciton line A have a certain analogy with the $y_1 \rightarrow y_0$ transition mentioned above (see Fig.5). The slight difference in the peak energies between the 6.2 eV exciton band observed for $E \perp c$ and that observed for $E \parallel c$, which is comparable to the energy difference between the structures B and B' of Fig.3 as mentioned in the preceding section, suggests that the high energy component appearing as a peak B in the LHeT ε_2 spectrum of Fig.3 is more active for $E \perp c$ than for $E \parallel c$ whereas the low energy component appearing as a structure B' in the LHeT spectrum has about equal transition proberbilities for both polarizations. This is in favor of the assumption that the 6.52 eV peak C is the second component of the exciton line B, since no structure is observed for $E \parallel c$ at this photon energy.

Stress experiments on these exciton lines are in progress to clear up the locations of their associated critical points and the origin of their strong exciton effects.

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