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*To be presented at the 6th Int. Conf. on High Pressure Physics to be held at Vancouver, B.C. Canada, Aug. 22-25, 1994.*

## **DEEP LEVELS IN AgGaSe<sub>2</sub>**

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### **ABSTRACT**

The photoluminescence spectra of AgGaSe<sub>2</sub> obtained at 77 K is reported. Two emission peaks have been observed and their pressure dependence studied. One of these peaks has been identified with emission involving one of the two deep level peak D<sub>1</sub> and D<sub>2</sub> observed previously in absorption measurement [*Appl. Phys. Lett.* 64,1717 (1994)]. A simple model for the capture of carriers into these deep levels has been proposed.

**KEYWORDS:** Semiconductors, Defects, Luminescence

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Recently we reported the pressure dependence of the absorption edge in  $\text{AgGaSe}_2$  at room temperature [1]. We observed below the bandgap two absorption peaks whose pressure coefficients are larger than that of the bandgap. Based on their pressure coefficients we proposed that these two peaks involved deep levels of an unknown nature. In the present work we report the 77 K photoluminescence spectra in  $\text{AgGaSe}_2$ . We observed two emission peaks. Based on their pressure dependence, we identified one of them with excitonic recombination while the other one we attributed to emission from one of the two deep levels. We found the pressure coefficients of these two peaks to be significantly reduced from their room temperature values. Based the pressure dependence of their relative intensities a schematic model for the trapping of carriers into these two deep levels in  $\text{AgGaSe}_2$  has been proposed.

The  $\text{AgGaSe}_2$  samples used in the present study were cut from the same bulk  $\text{AgGaSe}_2$  crystal used in our previous absorption [1] and Raman experiments [2,3]. The sample characteristics and preparation method and properties have been described before [1] and therefore will not be repeated here. Pressure was applied by a diamond anvil cell (DAC). A 4:1 mixture of methanol and ethanol was used as the pressure medium. The sample orientation is (112) and its thickness is about 50  $\mu\text{m}$ . After pressure was applied at room temperature, the DAC was cooled to near liquid nitrogen temperature via the cold-finger of an optical dewar. Pressure was determined by comparing the peak positions of the  $R_1$  fluorescence line of a Ruby chip placed, respectively, inside and outside the DAC [4]. The photoluminescence (PL) spectra were excited by a continuous wave Rhodamin 6G dye laser. Under pressure the appearance of the sample changes from opaque to transparent with an orange-red color, we have therefore increased the excitation laser photon energy with pressure to maximize the PL signal. The PL signals were analyzed by a SPEX double monochromator and detected by a single-channel photon counting system.

Figure 1 shows the PL spectra of our  $\text{AgGaSe}_2$  sample measured at 77 K at several different pressures. The original spectra contained also some sharp lines from the Ruby fluorescence. These lines could be easily distinguished from the sample PL by their different pressure dependence and had been removed from Fig. 1 for clarity. At atmospheric pressure we observed two peaks at 1.748 eV ( $14100 \text{ cm}^{-1}$ ) and 1.798 eV ( $14500 \text{ cm}^{-1}$ ). For brevity we shall refer to these peaks as A and B respectively. Artus and Bertrand [5] have determined from reflectivity the energies of the bandgap and exciton of  $\text{AgGaSe}_2$  at 77 K to be 1.83 and 1.81 eV respectively. From resonant Raman scattering studies performed on the same sample at

77 K and under ambient pressure [3], we have determined the energy of the free exciton in AgGaSe<sub>2</sub> to be 1.81 eV. Based on these results we identify the peak B at 1.798 eV as the recombination peak of either the free exciton or a very shallow bound exciton in AgGaSe<sub>2</sub>. We note that the full-width-at-half-maximum of this exciton peak is of the order of 50 meV. The corresponding widths of the resonant Raman enhancements are about a factor of 2 smaller. Both of these widths are large compared to the thermal energy  $k_B T$  (where  $k_B$  is the Boltzmann constant and  $T$  is the sample temperature). These rather large linewidths of the excitonic peak suggest considerable inhomogeneous broadening in our AgGaSe<sub>2</sub> sample.

Figure 2 shows the pressure dependence of the two PL peaks A and B. The straight lines drawn through the data points are least-squares fits to the experimental result. From these fits we obtained the pressure coefficients of the two peaks as: (A) 4.6 meV/Kb and (B) 3.8 meV/kb. We notice that peak B has a larger pressure coefficient than peak A. At room temperature we have found two absorption peaks  $D_1$  and  $D_2$  which have pressure coefficients larger than that of the fundamental absorption edge. These peaks occur at photon energies of about 50 and 120 meV, respectively, below the absorption edge. Since the separation between the two peaks A and B is also 50 meV, we have identified the peak A at 1.748 eV as due to emission from the deep level  $D_1$ .

If the above identifications are correct then it is necessary to explain the difference between the pressure coefficients for the bandgap and the deep level  $D_1$  measured at 77 K and at room temperature. The corresponding room temperature values measured by absorption have been reported to be: 5.1 and 6.9 meV/Kb respectively [1]. The room temperature pressure coefficient for the bandgap is in good agreement with the value of 5.3 meV/Kb reported by Jayaraman et al. [6]. The reduction in the bandgap pressure coefficient between room temperature and low temperature is about 24%. One possible explanation is a stiffening of the lattice with decrease in temperature. The pressure coefficient  $dE_g/dP$  of an energy gap  $E_g$  can be expressed as:

$$\frac{dE_g}{dP} = \left(\frac{dE_g}{dV}\right) \left(\frac{dV}{dP}\right) = \left(\frac{dE_g}{dV}\right) \beta V \quad (1)$$

where  $V$  is the volume of the crystal and  $\beta = V^{-1}(dV/dP)$  is the compressibility. If the compressibility of AgGaSe<sub>2</sub> increases as temperature is decreased while the volume coefficients ( $dE_g/dV$ ) for its energy gaps are independent of temperature, then we expect that the pressure coefficients of all the energy gaps of AgGaSe<sub>2</sub> will change by the same percentage as a function

of temperature. For the level  $D_1$  we found that its pressure coefficient also decreased by a large amount (33%) between room temperature and 77 K. Thus it is quite likely that a compressibility which decreases by about 25%-30% with temperature is responsible for the difference between the room temperature and 77 K pressure coefficients for the bandgap and the deep transition  $D_1$  in  $\text{AgGaSe}_2$ . This explanation awaits direct confirmation by temperature dependent x-ray measurements on  $\text{AgGaSe}_2$  under pressure.

We note in Fig. 1 that at atmospheric pressure the peak A is only slightly weaker than peak B although the corresponding oscillator strength of the peak  $D_1$  in absorption is much weaker than that of the bandgap [1]. This difference can be explained by the much larger photoexcited population in level  $D_1$  because of its lower energy. In Ref. 1 we have suggested that the peak  $D_1$  is associated with a bound-to-bound transition involving a deep donor and deep acceptor. Its recombination peak will be enhanced with respect to that of the intrinsic excitonic peak because of the larger population of photoexcited carriers trapped at these lower energy deep levels. However, as pressure decreases their energy separation, peak A grows rapidly relative to peak B until peak B becomes a weak shoulder at pressures above 26 Kbar. This is contrary to expectation if we assume that the ratio of the intensities of peak B to peak A should vary with their separation ( $\Delta E_{AB}$ ) as  $\exp(-\Delta E_{AB} / k_B T)$  where  $k_B$  is the Boltzmann constant and T is the sample temperature. Thus our result suggests that pressure must increase the probability for carriers to be trapped at the deep centers. One possibility for this to happen is that there is a *barrier to capture* into the  $D_1$  level and it *decreases* with pressure. We also note that the level  $D_2$ , which has even lower energy than the level  $D_1$ , is not observed at all in emission, although in absorption the peaks  $D_1$  and  $D_2$  have comparable strength [1]. To understand this result we suggest that there is also a barrier to the capture of photoexcited carriers into the deep levels  $D_2$  and its height is much larger than that for level  $D_1$ . As a result the population of carriers trapped at  $D_2$  is much smaller than in  $D_1$  at 77 K. At room temperature, on the other hand, carriers have sufficient energy to overcome the barrier heights to be trapped with comparable probabilities at both levels. A schematic diagram of our model is shown in the inset of Fig. 2.

Finally, we observed a sudden change in the PL of  $\text{AgGaSe}_2$  at  $P=77$  Kbar just before the onset of a structural phase transition. It has been reported by Carlone et al. [7] that  $\text{AgGaSe}_2$  underwent phase transformations at 42 and 116 Kbar. By optical observation at room temperature we have found evidence of a phase transformation at  $60 \pm 5$  Kbar in  $\text{AgGaSe}_2$ . At

this pressure the sample changed from orange-red in color to opaque. At low temperatures we found that this phase transformation pressure is increased to  $P \geq 80$  Kbar. This increase in transition pressure in  $\text{AgGaSe}_2$  at 77 K is consistent with its smaller compressibility at low temperature proposed earlier. In Fig. 3 (a) and (b) we compare the PL of  $\text{AgGaSe}_2$  measured at 52 and 77 Kbar respectively. At 52 Kbar the PL spectra is dominated by one strong peak at 2.0 eV ( $16120 \text{ cm}^{-1}$ ) corresponding to the unresolved peaks A and B. However, at 77 Kbar this unresolved PL peak (labeled A+B in Fig. 3 (b)) has become a very weak shoulder riding on the laser line (the laser frequency has to be changed to enhance the PL intensity at 77 Kbar). On the other hand a new broad and strong peak appears at 1.7 eV ( $13700 \text{ cm}^{-1}$ ). We attribute this new peak to emission associated with an opaque high pressure phase of  $\text{AgGaSe}_2$ .

In conclusion we have observed two emission peaks in the PL spectra of  $\text{AgGaSe}_2$  and studied their pressure dependence. One of these peaks has been identified with emission from the deep level peak  $D_1$  observed previously in absorption. A simple model for the capture of carriers into these deep levels has been proposed.

#### ACKNOWLEDGMENTS

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## FIGURE CAPTIONS

Figure 1. Photoluminescence spectra of  $\text{AgGaSe}_2$  as a function of pressure at 77 K.

Figure 2. Pressure dependence of the peak energies of the peaks A (open circles) and B (solid circles) observed in the photoluminescence spectra of  $\text{AgGaSe}_2$ . The solid lines are least-square fits to the experimental points. The inset is a schematic model of the capture barrier height for carriers into the deep levels  $D_1$  and  $D_2$ .

Figure 3. The PL spectra of  $\text{AgGaSe}_2$  at (a) 52 Kbar and at (b) 77 Kbar. The peak label A+B is the sum of the unresolved peaks A and B shown in Figs. 1 and 2.

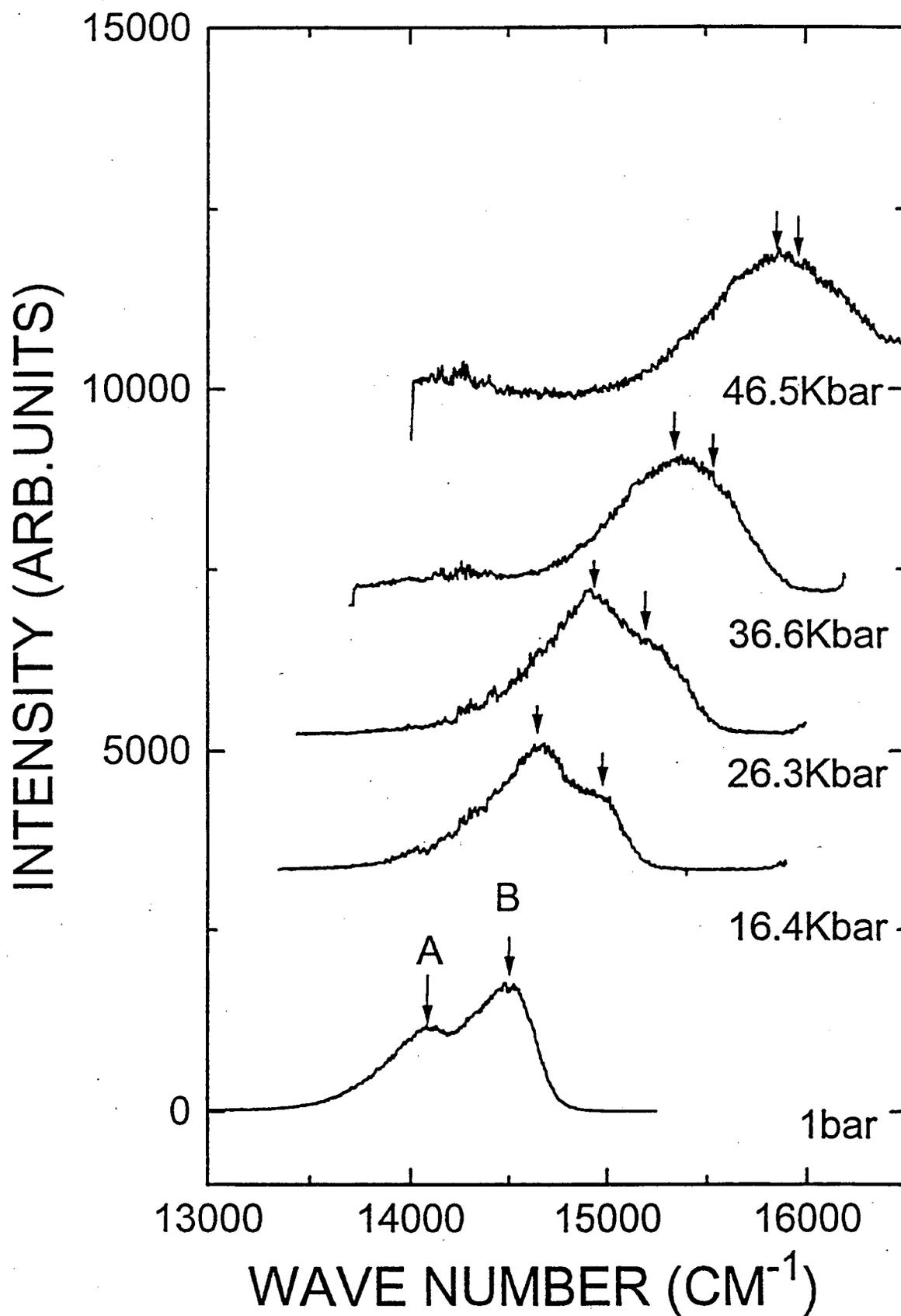


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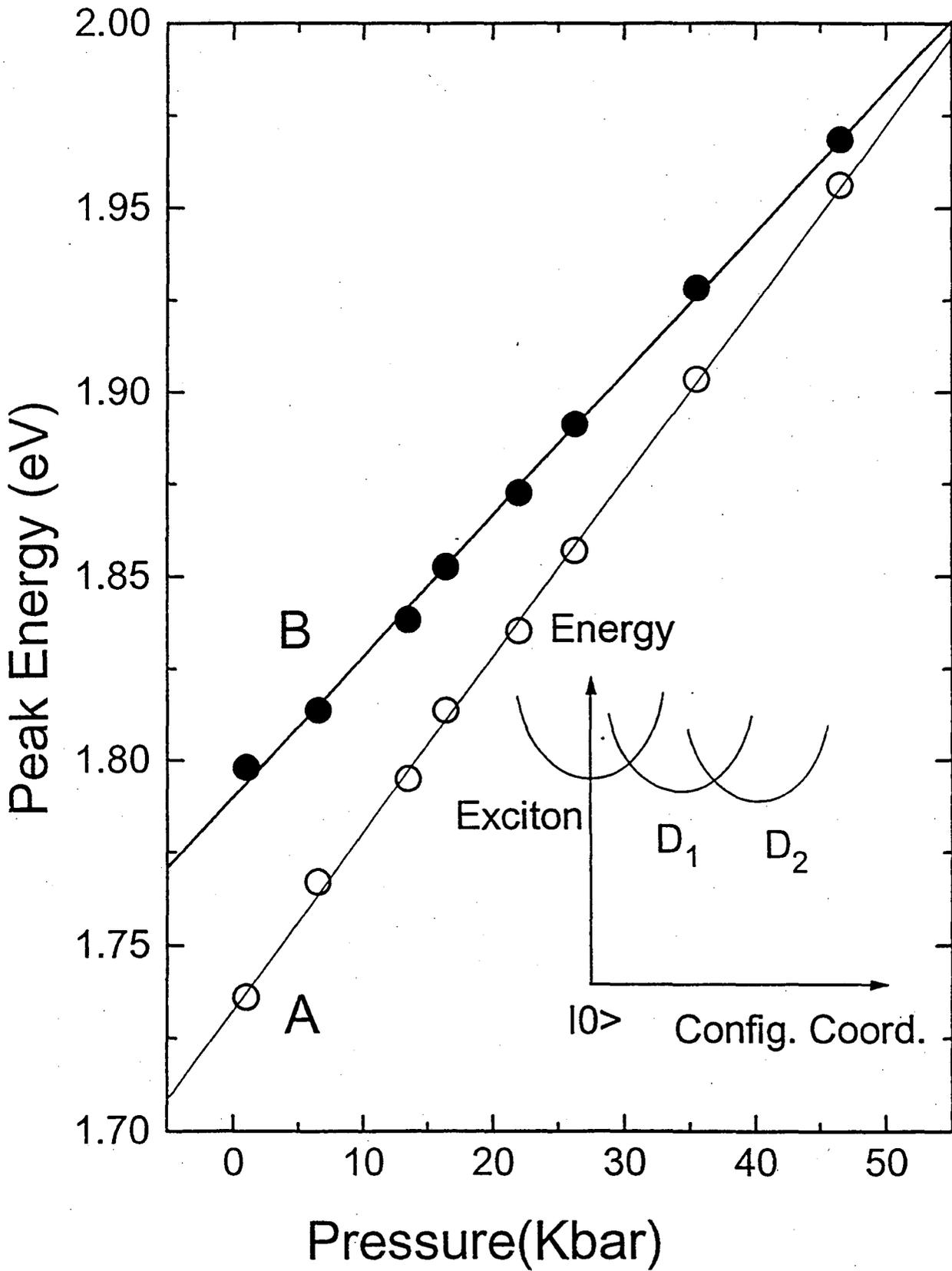
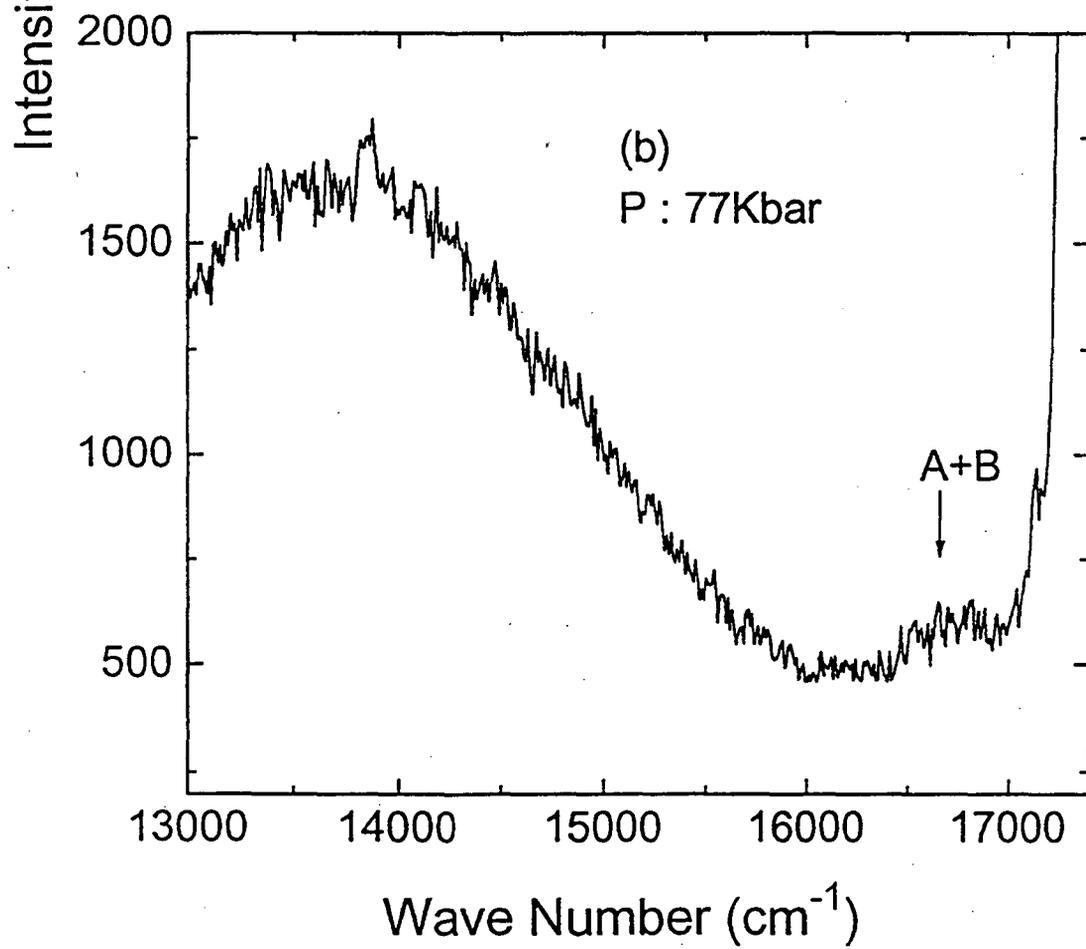
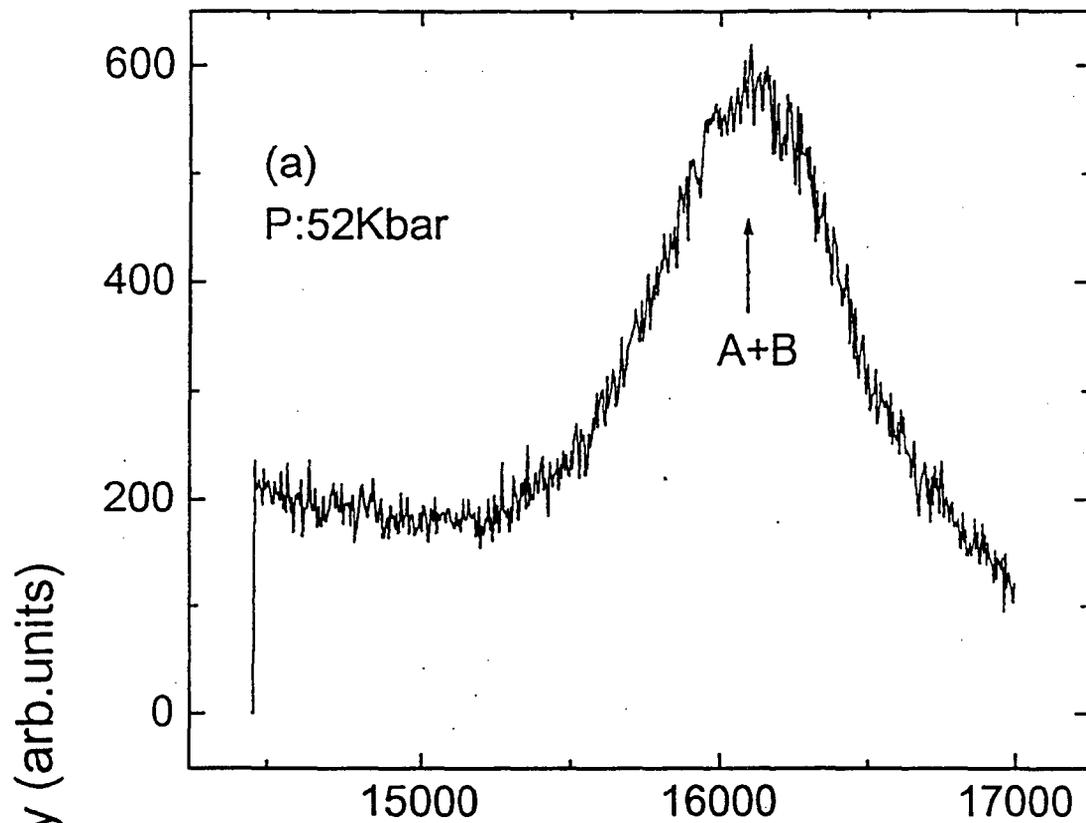


Fig. 2 Choi and Yu



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