

Low-temperature photoacoustic spectra of BiI_3 single crystals

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The photoacoustic (PA) spectra of layer halide BiI_3 has been studied by a piezoelectric transducer as a detector in the temperature region from 115 K to room temperature. Four peaks of G (1.97 eV), A (2.03 eV), B (2.17 eV), and C (2.38 eV) are observed in the PA spectra at 115 K. Peaks A and B are explained by the transition of the ground and the first excited states of the direct exciton. The onset of the transitions from the spin-orbit split valence band occurs at peak C . The decrease of the PA signal which begins at peak C is interpreted by the generation of the different pathways for the relaxation of the excited carriers. Since the intensity of the peak G varies from sample to sample and the peak has not been observed in the photoluminescence measurements, the origin of the peak G is attributed to the nonradiative transitions of the extrinsic centers. This capability to observe the nonradiative-decay processes is one of the chief advantages for the PA measurements.

I. INTRODUCTION

The photoacoustic (PA) spectroscopy for solid materials has been revived in the seventies and has been used to investigate physical properties of semiconductors.¹ The basic concept of the PA measurement is as follows. Light absorbed by the solid will excite a fraction of the ground states into higher energy states. These excited states will subsequently relax through a combination of radiative and nonradiative pathways. The nonradiative component will ultimately generate heat in the localized region of the sample and generate a pressure or an elastic wave that propagates away from the heat source. The pressure or the elastic wave is then detected as a PA signal by a suitable sensor such as a microphone or a piezoelectric transducer. There are advantages for the PA spectroscopy over the other conventional optical measurements. One of the principal advantages is that it enables us to obtain spectra, similar to the optical absorption spectra, on any type of solid or semisolid materials, whether it be crystalline, powder, or gels. And the PA detection is unique in that it can be a direct monitor of the nonradiative relaxation channel. Therefore, the PA technique may complement absorption and photoluminescence spectroscopic technique.

In the conventional PA spectroscopy, the heat generated by the absorption of light is coupled to a nonabsorbing gas and a time-dependent pressure fluctuation is detected by a highly sensitive microphone. An alternative PA measurement has been developed by Jackson and Amer² utilizing a piezoelectric transducer attached directly to a sample. Since the transducer has a wide frequency response and can be used over a wide range of temperature and pressure, the transducer method will be

more suitable for the low-temperature PA measurement of the semiconductors.³

We have already carried out the low-temperature PA measurements on the layer semiconductors InSe (Ref. 4) and GaSe.⁵ For both semiconductors, the PA signals due to the annihilation of the direct free exciton have been clearly resolved. And the discussion for the nonradiative impurity centers, which had been reported for the first time, were developed. We have also demonstrated that the low-temperature PA spectra would give a very useful insight to the electronic transitions, both radiative and nonradiative, in the semiconducting materials.

BiI_3 crystallizes in a structure which was derived from the octahedral CdI_2 -type layer structure, which consists of three close-packed atomic sheets per layer in the sequence of anion-cation-anion. Modification occurs in which only two-thirds of the usual sites in the cation sheets are occupied.⁶ The first interest of the optical properties of BiI_3 might be due to the possible technical application as a new material for photographic processes.⁷ A proposition of a bihole or a bielectron model for BiI_3 to interpret a series of lines in the absorption spectra have stimulated a further attention to study the optical properties.⁸ Optical measurements of BiI_3 single crystals including an absorption and photoluminescence spectra have been studied by many authors recently.⁸⁻¹² Direct exciton transition near 2.0 eV at room temperature has been well established, and the indirect exciton band which lies very close in energy to the direct one has been studied. The steplike structures have been observed in the absorption spectra only below the temperature of about 20 K.¹¹ These structures are well interpreted by the indirect optical transition with phonon

emission and absorption. The observed phonon energies are in good agreement with that obtained from the Raman scattering measurements. The energy position of the indirect exciton band is 2.0081 eV at 1.8 K and the average temperature coefficient of this band is $+1.0 \times 10^{-4}$ eV/K, which has an opposite sign to that of the direct exciton band.¹² At temperatures higher than about 20 K, the steps due to the indirect transitions are successively superimposed by an intense continuous absorption of direct exciton band. For the sharp absorption lines observed below the fundamental absorption edge, an extrinsic origin has been evidenced.¹²

For the PA study of BiI_3 , only one spectra at room temperature has been observed by using a microphone technique by Fernelius.¹³ He has estimated the band edge of 1.91 eV from the PA spectra, but no detailed discussion were presented. In this paper we report for the first time on the PA spectra of BiI_3 at low temperatures by using a piezoelectric transducer as a detector. The origins of the observed PA peaks are discussed in detail by comparing them with the optical absorption spectra.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The single crystals of BiI_3 were grown in the two-zone electric furnace by a vapor transport technique with excess iodine as a transport agent. The platelet single crystals with typical dimensions of $5 \times 5 \times 0.05$ mm³ were obtained in the cold end of the sealed ampoule. The x-ray diffractometer measurement showed that the crystals belong to the rhombohedral structure and the major surface of the platelet is a rhombohedral (111) plane (*c* plane in the equivalent hexagonal unit cell). The *c* plane was easily cleaved by an adhesive tape and the freshly cleaved samples were always used for the measurements. Care was taken not to introduce any bending forces to the sample.

The details of the experimental setup for the low-temperature photoacoustic spectroscopy have already been reported.³ We have used a sputtered ZnO film as a piezoelectric transducer for the PA signal detection in the preceding works for the layer semiconductors InSe (Ref. 4) and GaSe.⁵ The samples must undergo heat treatments three times to fabricate the sputtered ZnO films with vacuum evaporated aluminum electrodes. The melting point of BiI_3 is approximately 440°C.⁹ The color of the sample surface slightly changed by these heat treatments and reproducible results of the PA spectra could not be obtained by the ZnO transducer. Therefore, we used a commercially available piezoelectric transducer NPM (Tokin Co., type N21), which is less sensitive than ZnO films,³ as a detector for the PA measurements of BiI_3 . The thickness and the diameter of the NPM are 0.15 and 7 mm, respectively.

To obtain a PA signal, we used two types of the detector geometry. One is by a ring-shaped (annulus) and another is by a disc-shaped NPM. The schematic geometries of the samples and the detectors using the ring- and the disc-shaped NPM are drawn in the insets of Figs. 1 and 2, respectively. The samples were carefully glued onto one side of the NPM detector by using

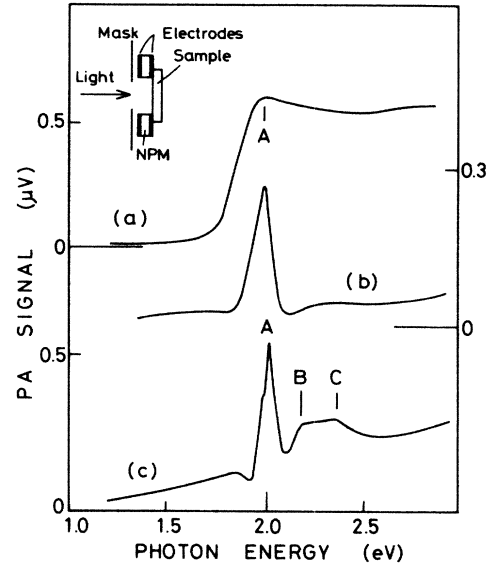


FIG. 1. The temperature variation of the PA spectra of the BiI_3 sample taken from sample batch No. 3. The measured temperatures are 290 (a), 165 (b), and 117 K (c). The ring-shaped NPM was used as a detector and the detector geometry is shown in the inset.

silver conducting paint to obtain a good thermal and mechanical contact. The generated signal voltages were measured by two electrodes which were attached to both surfaces of the detector. The light was always incident on the crystallographic *c* plane of the sample and the electric field vector of the light is in the plane ($E \perp c$). In the case of the ring-shaped NPM, the light was incident

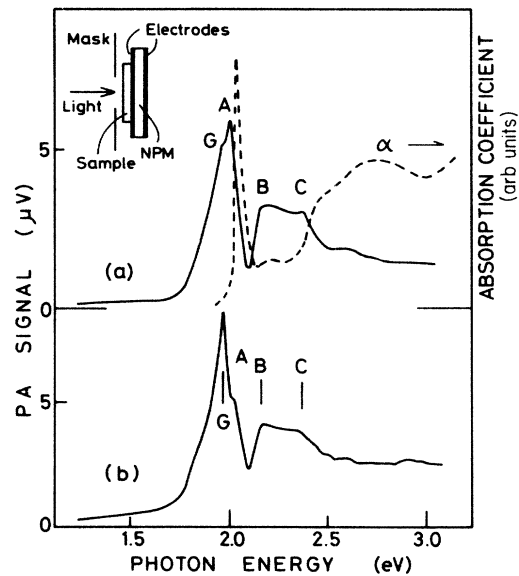


FIG. 2. The PA spectra at 115 K of the other BiI_3 samples taken from sample batch No. 3 (a) and batch No. 4 (b). The disc-shaped NPM was used as a detector and the detector geometry is shown in the inset. The absorption spectra at 77 K obtained from the reflectance measurements (Ref. 12) is superimposed by the dashed curve on the PA spectra.

on the detector side of the sample through the hole of the detector. Suitable mask was used to prevent the light to illuminate the piezoelectric detector. In the case of the disc-shaped NPM, the light illuminated the opposite side of the sample to the detector.

The temperature variation of the PA spectra of BiI₃ is shown in Fig. 1. Practically observed PA signal voltages are shown in the ordinate of the figure. They are all less than 0.5 microvolts and the signal intensities are in a same order from 117 K to room temperature. The PA signals were normalized by the intensity of the incident light. The ring-shaped NPM was used as a detector and the incident light illuminated on the NPM side of the samples. The thickness of the samples was 30 μm. Figure 1(a) is a PA spectrum at room temperature (290 K). As the incident photon energy $h\nu$ increases, the PA signal intensity begins to rise gradually near 1.75 eV and shows a maximum at 1.98 eV. Hereafter we refer this peak as peak *A*. The spectral shape of the lower-energy side of this maximum was well fitted by a Gaussian distribution function. Above this maximum, the spectra show a plateau up to $h\nu$ of 3.0 eV with a small hump around 2.5 eV.

When the temperature decreases to 165 K, a large peak appears at 2.0 eV in Fig. 1(b). Useful structures could not be observed in the $h\nu$ region above this peak. A further decrease of the temperature down to 117 K makes the peak narrower as shown in Fig. 1(c). Additional structure at $h\nu$ just below that of peak *A* is observed. In the plateau region above peak *A* of 2.03 eV, two shoulders at 2.17 eV (labeled as peak *B*) and at 2.38 eV (as peak *C*) appear.

Figure 2 shows the PA spectra at 115 K for other samples of BiI₃. One, in Fig. 2(a), was taken from the same batch (No. 3) as that in Fig. 1. Another, in Fig. 2(b), was from a different batch (No. 4). In the case of Fig. 2, disc-shaped NPM transducers were glued to the the sample and the light was incident on the opposite side of the sample to the detector. The thicknesses of the samples were 18 and 22 μm for Figs. 2(a) and 2(b), respectively. The overall features of the spectra were the same as that in Fig. 1 in the temperature range from 115 K to room temperature (not shown in the figure). The ordinate shows practically observed PA signal voltages. The observed signal intensities are about ten times larger than that in Fig. 1. The structures in the spectra at *B* and *C* peak positions become more clear. The large peak (labeled *G*) clearly appears very near peak *A*. The energy position of peak *G* is 1.97 eV. The intensity ratio of peak *G* to peak *A* is greater than unity for the samples taken from batches No. 1, No. 4, and No. 5 and is less than unity for No. 2 and No. 3. Even in the samples taken from the same batch, the intensity ratio slightly varies from sample to sample.

III. DISCUSSIONS

The fundamental theory of a piezoelectric PA spectroscopy has been developed by Jackson and Amer² for the condensed matter samples. Consider a platelet crystal sample. When the light is incident on the center of

the platelet sample, the temperature of the illuminated volume increases, leading to an expansion of that region as well as an out flow of the heat. In the case of a weakly absorbing solid, the enlargement of the central region causes the general expansion of both the front and rear surfaces of the sample. But in the case of a strongly absorbing solid, the heat in the illuminated region decays spatially through the thickness of the sample. Consequently, the front position of the sample expands more than the rear, resulting in a bending of the sample. Such bending compresses the rear surface of the solid and oppose the general expansion.

The observed PA signal intensity, therefore, strongly depends on the absorption coefficient α of the solid sample.² For the small value of α , the PA signal is directly proportional to α . For the high value of α , the position of the piezoelectric transducer with respect to the direction of the incoming beam yield significantly different results. When the transducer is away from the beam, this is the case for Fig. 2 in our experiments, the signal decreases with the increase of α and eventually passes through zero changing the sign near $\alpha L \sim 2$, where L is the sample thickness. The compression by the bending exceeds the expansion at the rear side of the sample due to the heating. On the other hand, when the ring-shaped transducer is attached to the sample surface toward the incident beam, as for Fig. 1, the PA signal shows little saturation until αL reaches high value. The bending and expansion term combine thus increasing the observed signal. Since the absorption coefficient of BiI₃ at the photon energy near 2.0 eV is an order of $2 \times 10^3 \text{ cm}^{-1}$,¹² the value of αL exceeds an order of 100 in both cases of Figs. 1 and 2. According to the predictions by Jackson and Amer,² the PA spectra of BiI₃ above 2.0 eV in the strongly absorbing region should be significantly different between Figs. 1 and 2. But it is not the case for our experimental results. The spectra are almost the same for both detector geometries.

The disagreement between the experimental results and the theoretical predictions may be due to the breakdown of the two assumptions by Jackson and Amer.² First, they have assumed that the sample was thick compared to the transducer and the transducer was compliant. The thickness of the NPM detector was about six times larger than that of the sample in the present case for BiI₃. Second, a pyroelectric effect has been neglected. If the significant amount of heat is transmitted to the transducer, the transducer would develop thermal stresses of its own and produce a voltages due to the pyroelectric effect. More elaborate studies are necessary to fit the experimental data to the theoretical predictions for the piezoelectric PA measurements.

Since the observed PA spectra by the two very different detector geometries are the same, we can consider that the observed PA spectra directly reflect the spectra of absorption coefficient. This hypothesis is also justified by the fact that the PA spectra at room temperature, Fig. 1(a), is the same as the absorption spectra reported in the literature. The details are discussed in the following.

A difference between the spectra of Figs. 1 and 2 was

their observed signal intensity. The signal obtained by using the disc-shaped NPM is more than ten times larger than that of the ring-shaped one. This may be partly due to the difference of the contact areas between the sample and NPM detectors. The contact area is larger in the disc-shaped NPM and gives a larger signal intensity. Therefore, we could obtain more reliable PA spectra at low temperatures when we used the disc-shaped NPM.

For the PA spectral study of BiI₃, only one report has been published by Fernelius.¹³ He has obtained the room-temperature PA spectra for the BiI₃ disk sample, not a single crystal, by using a gas cell and a microphone as a detector. The observed spectra show an absorption edge of 1.91 eV (650 nm), and he concluded that by using a PA spectroscopy one could routinely obtain absorption edges on highly absorbing materials without resorting to any special sample preparation procedures. No detailed discussion has been given on the saturation of the PA signal as the increase of the absorption coefficient α , which is one of the important factors to determine the absorption edge from the PA spectra for highly absorbing solids.¹

In the PA spectra at room temperature in Fig. 1(a), a maximum was observed at 1.98 eV. The absorption spectra of BiI₃ single crystals has been obtained from the optical reflection measurements by using a Kramers-Kronig dispersion relation.¹² The maximum of the absorption spectra at 286 K was observed at 1.97 eV and the spectral shape of the absorption spectra is almost the same as that of the PA spectra. This fact ascertains our assumption that the PA spectra directly reflect the absorption spectra. It is then considered that the origin of peak *A* is explained by the transitions of the direct excitons as in the case of the absorption measurements. Peak *A* becomes narrower and the energy location of the peaks shift toward the higher-energy region by decreasing the temperature.

At 115 K, the PA spectra of Fig. 2 consists of four peaks labeled *G* (1.97 eV), *A* (2.03 eV), *B* (2.17 eV), and *C* (2.38 eV). To discuss the origin of these peaks in more detail, it would be helpful to compare the PA spectra with the absorption spectra in the literature. The absorption spectra at 77 K obtained by Kaifu *et al.*¹² is superimposed by the dashed curve on the PA spectra at 115 K of Fig. 2(a). Two dominant absorption peaks at 2.072 and 2.210 eV at 77 K correspond to the PA peaks *A* and *B* at 115 K, respectively. Compared to the absorption peaks, the energy location of peaks *A* and *B* are both shifted toward the lower-energy region by the temperature effect. The rise up of the absorption coefficient near 2.4 eV also relates to peak *C*. However, no corresponding signal to peak *G* was observed in the absorption spectra. We then discuss the origin of the observed peaks in the PA spectra by referring to the information of the absorption spectra.

As mentioned before, peak *A* was due to the $n = 1$ excitonic transitions. Excitonic peak *A* at 2.03 eV was attributed to M_0 -type van Hove singularity at the *A* point of the Brillouin zone on the basis of the band model.⁶ An uppermost valence band is arising from the iodine *5p*

state with a strong admixture of bismuth *6s* state, and a conduction band is built up by Bi *6p* states. This means that the excitons near the fundamental absorption edge have a cationic character as in the case of PbI₂.¹⁴ The temperature dependence of the energy of peak *A* was estimated as -2.9×10^{-4} eV/K and is in agreement with the values of -2.6×10^{-4} by Evans⁹ and -3.4×10^{-4} eV/K by Komatsu and Kaifu.¹⁰ If we consider that peak *B* is due to the first excited state ($n = 2$) of the excitonic states, the binding energy of the excitonic is estimated as 190 meV. Using 6.176 for the dielectric constant,⁹ the $n = 1$ exciton orbit diameter was evaluated to be about 6 Å. Since the layer thickness of the BiI₃ crystals is 6.9 Å, the orbit of the $n = 1$ exciton may be confined onto one layer.

The valence band of BiI₃ was partly formed from the *5p* orbitals of the iodine ions and consequently should be split into two levels ($j = \frac{1}{2}, \frac{3}{2}$) by a spin-orbit interaction.⁹ If peak *C* is due to one of these split valence bands, the energy separation is estimated as 0.35 eV. This is agreed with that reported by Evans.⁹ For the other group-V metal halide SbI₃, the $n = 1$ exciton band appeared at 2.572 eV (77 K) and the spin-orbit splitting energy of 0.37 eV was observed for the thin-film samples.¹⁵ The similarity of the value of the splitting energy between SbI₃ and BiI₃ means that the splitting mainly arises from the iodine ions. The metal ions do not strongly affect the splitting as long as the spin-orbit interaction of the iodine atoms do. Although the absorption peak due to the spin-orbit splitting of the *p*-like Bi conduction band has appeared at 3.8 eV,¹⁰ this is beyond the measured photon energy region of our experiments.

When the additional interband electron transitions occur, the absorption coefficient should increase at the critical photon energy as shown by the dashed curve in Fig. 2(a). But the PA signals begin to decrease at peak *C* (2.38 eV) where the electrons earn sufficient energy to be excited from the spin-orbit split off valence band. Similar behavior has been seen in the PA spectra of Ga_{1-x}Al_xAs heterostructures.¹⁶ The decrease of the PA signal at the indirect transition which merged in the absorption continuum of the direct transition has been reported. The PA effect was due to the heat generation by the nonradiative energy decaying process of the optically excited carriers in the semiconductor. Therefore, the induced PA signal would change at excitation photon energies where the carriers are excited to the energy states of another interband transition. If these energy states have different pathways for the relaxation of the excited carriers, where the radiative transition becomes dominant to the recombination, the decrease of the PA signals amplitude would be expected. Accordingly, we can attribute the origin of peak *C* to the onset of the transitions from the deeper valence band, which was split off by the spin-orbit interaction, to the conduction band.

Next, we consider the origin of peak *G* at 1.97 eV which was observed for the first time by the PA measurements in the lower-energy region than the energy location of peak *A*. Since the intensity of peak *G* compared with that of *A* varies strongly from sample to sample, it is considered that peak *G* has an extrinsic ori-

gin. The extrinsic optical processes near the indirect exciton band edge have been evidenced by Kaifu *et al.*¹² It consists of a set of sharp peaks beyond the $h\nu$ of 1.986 eV at 1.8 K. And their presence strongly depends on the sample. It is considered that the layer structures of BiI₃ easily allow the introduction of a stacking fault due to a weak van der Waals atomic bonding perpendicular to the layer. As a consequence of the distortions of the interlayer interactions at these stacking faults, the electronic states may be perturbed. The excitons which are bound to crystallographically nonequivalent layers have different energies giving rise to the sharp absorption lines in their observed spectra. And the temperature shifts of these absorption peaks were parallel to that of the indirect exciton band.^{11,17} Since the indirect band edge has a positive temperature dependence as discussed before, the rise of the temperature shifts these peaks to the higher photon energy region. This means that the peaks due to the bound exciton to the stacking fault do not contribute to the observed peak in our experiments. The largeness of the observed signal intensity compared with that of the intrinsic direct transition also supports this conclusion.

The absorption band at 1.93 eV has been observed in the absorption and luminescence spectra at 4.2 K. Petroff *et al.* considered that this band was associated with the impurities or the vacancies in the crystal.⁸ Similar absorption bands at 1.93 eV have been reported by Kaifu *et al.* and the bands were attributed to the defect centers.¹¹ Since it has been considered that the band at 1.93 eV is accompanied with the direct exciton band, this band should shift to the lower-energy region when the temperature increases. Therefore, we consider that peak *G* at 1.97 eV in Fig. 2 does not have the same origin as that discussed here.

As suggested before, peak *G* should have an extrinsic origin. This was because the PA signal intensity of the *G* peak strongly depends on the sample. Since no signal corresponding to this peak has been observed in the photoluminescence measurements,⁹ the extrinsic state associated with peak *G* in the PA spectra is considered to be a nonradiative center. Peak *G* is due to enhancement of the nonradiative recombination. The capability to ob-

serve such nonradiative-decay processes is one of the chief advantages of the PA measurements. Further studies for impurity- or defect-controlled samples will be necessary for detailed discussion.

In the PA spectra at the temperatures above 165 K, no peaks except peak *A* were observed. The structures of the spectra such as peaks *B*, *C*, and *G* should smear out at higher temperatures. The PA signal intensity in the photon-energy region of peaks *B* and *C* was unexpectedly small compared with that of peak *A* at 165 K. The reason is not clear at present.

IV. CONCLUSION

In this paper we reported the low-temperature PA spectra of layer halide BiI₃. By comparing the PA spectra obtained by the two different types of detector geometries, it became clear that the observed PA spectra directly reflected the absorption spectra for highly absorbing BiI₃ crystals. Four peaks were observed in the spectra at 115 K. The first peak *G*, which was found in the lowest-energy region of the spectra, arose from extrinsic states such as impurities or defects. Since no corresponding peak was observed in the photoluminescence spectra, the transition which causes peak *G* is considered to be a nonradiative process. The nonradiative center of BiI₃ could be observed for the first time by the PA technique.

The second and the third peaks (peaks *A* and *B*) are due to the ground and first excited states of the direct excitons, respectively. For the last one (peak *C*), it was considered that the spin-orbit split valence bands have an important role to the transition. The decrease of the PA signal at the energy position of peak *C* was explained by the occurrence of the different pathways for the relaxation process of the excited electrons.

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