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Transmittance Spectra and Optical Constants of Alkali-Antimony Compounds K₃Sb, Na₃Sb, and Na₂KSb

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Measurements of the transmittance spectra of alkali-antimony compounds K_3Sb, Na_3Sb, and Na_2KSb, carried out from 0.5 to 6.2 eV at room temperature, are analyzed by the Kramers–Kronig dispersion relations to yield the refractive index and the extinction coefficient. The refractive index at photon energies less than the lowest band gap is about 2.0 for these compounds. The $\epsilon_2(\omega)$ curve shows two pronounced peaks at 2.3 and 3.45 eV for hexagonal K_3Sb and at 2.7 and 3.6 eV for cubic K_3Sb, whereas it shows only one pronounced peak at 2.5 eV for Na_3Sb and at 3.05 eV for Na_2KSb.

I. INTRODUCTION

Because of their high-photoemissive properties, Cs_3Sb and multialkali antimonide $Na_{3-x}K_xSb$ are well-known and widely used photoemissive compounds. In an earlier paper,[1] the refractive index and the extinction coefficient have been reported for Cs_3Sb. For the other alkali-antimony compounds, these two sets of the optical constants have not been reported, despite the many publications concerning photoemission, light absorption, photoconductivity, and crystal structure. These publications were summarized by Sommer.[2] Transmittance properties of K_3Sb have been investigated quite extensively by Spicer,[3] Taft and Philipp,[4] and Sommer and McCarroll.[5] In a recent paper,[6] hereafter referred to as I, we have presented the preliminary determination of the optical constants of purple K_3Sb using a Kramers–Kronig (KK) dispersion analysis of the transmittance data. The present paper describes detailed optical properties of K_3Sb; this compound has two modifications, the purple hexagonal and the brown cubic form.[5] The optical constants of Na_3Sb and Na_2KSb are also presented. The results provide the important information needed for the future systematic study of the electronic structure of alkali-antimony compounds.

II. EXPERIMENTAL PROCEDURE

A. Materials Preparation

The preparation of K_3Sb was presented in I, so that only a brief description is given here. Antimony is evaporated on a quartz substrate of 1-mm thickness at a pressure of less than 1×10^{-6} Torr. The evaporated Sb film is then exposed to K vapor at 160 °C until peak sensitivity to white light is obtained. At the photosensitivity peak, the resistance decreases to a value of two or three orders of magnitude less than the peak value. The film shows pure purple color in transmitted light. On the basis of the transmittance spectrum, this film is believed to be K_3Sb of hexagonal structure. In fact, it has been reported that the K-Sb system has the chemical composition of K_2Sb at the resistance peak[7] and K_3Sb at the photoemission peak.[5] The K_3Sb film thus obtained is n type, in agreement with previous work.[3,5,7] Thus conductivity type was determined by a thermoelectromotive-force measurement. It has been suggested that n-type conductivity is due to the stoichiometric excess K metal.[5] When the activation process of the evaporated Sb film with K vapor is continued beyond the photoemission peak, the resistance continues to decrease by about one order of magnitude and then it shows no change or only a very slow in-

crease with continued exposure to K vapor. In this case, the film shows brownish-purple color, but the conductivity type is unchanged.

By cesiation of purple K_3Sb with Cs-ion bombardment, the film color was changed unexpectedly from pure purple to brown: 6-eV Cs ions are absorbed up to one monolayer. This change in color is not ascribed to the optical absorption by absorbed Cs, because the absorption due to a monolayer of Cs is expected to be very weak compared with the absorption intensities studied in this work. In fact, the cesiation up to one monolayer using an ampoule containing Cs metal did not change the transmittance spectrum of purple K_3Sb at all. The transmittance spectrum of the film cesiated by ion bombardment is somewhat similar to that of cubic brown K_3Sb reported by Sommer and McCarroll.[5] These authors obtained brown K_3Sb by exposing the Sb film to a glow discharge in oxygen prior to the reaction with K. The role of oxygen, however, has not been made clear. An x-ray analysis has indicated that brown K_3Sb has cubic structure.[5] Although we are still uncertain about the crystal structure of our brown and brownish-purple films, optical measurements and the analysis of the transmittance data are made for these films. The analysis for cubic K_3Sb, for which transmittance data have been reported in Ref. 5, is also made, where the sample of those authors is denoted as cubic K_3Sb. Moreover, the analysis is made on the purple film of those authors, which is referred to as hexagonal K_3Sb. More detailed analysis for purple K_3Sb than that reported in I is also made.

The Na_3Sb films were prepared by a procedure similar to that used for purple K_3Sb except that the evaporated Sb film was exposed to Na vapor at 205°C. Similar to the case of K_3Sb films, the resistance increases very steeply when the Sb film begins to react with Na vapor, reaches a peak, and then decreases. The activation of the Sb film with Na vapor is stopped when the resistance decreases to a value of two or three orders of magnitude less than the peak value. The photoemission of Na_3Sb was not measured during the activation process, because Na_3Sb is not photosensitive to white light. The structure in the transmittance spectra of different Na_3Sb films are in good agreement with each other. The conductivity of Na_3Sb is n type determined from a thermoelectromotive-force measurement, in agreement with previous results.[3,8]

A simple method was employed for the preparation of the $Na_{3-x}K_xSb$ films, although more complex methods have been reported.[2] First the Sb film is exposed to Na vapor at 205°C. Care must be taken to stop this activation process when the resistance decreases to a value of one order of magnitude less than the peak value, or highly photo-

sensitive films are never formed. Following this procedure, the film is exposed to K vapor at 160°C, until peak sensitivity to white light is obtained. During the exposure to K vapor, the resistance continues to decrease, goes through a minimum, and then increases again. By this simple method, the photosensitivity as high as 60 μA/lumen is obtained with a reproducibility of 80%. This sensitivity is comparable to the previously reported value[9] obtained by the more complex method than that mentioned above. According to Ref. 10, the cubic phase Na_2KSb always predominates in the composition of the highly photoemissive Na-K-Sb system. Therefore, we assume that the composition of the highly photosensitive samples are mainly Na_2KSb with cubic structure. The p-type conductivity which was determined by measurements of a thermoelectromotive force also indicates that the Na_2KSb phase is predominant in the highly photosensitive samples. The crystal structure of Na_2KSb is given by MaCarroll[10] and by Scheer and Zalm.[11]

B. Transmittance Measurements

The transmittance was measured using a Cary model 14 spectrophotometer and a Shimazu IV-50A spectrophotometer in the photon energy region 0.5–6.2 eV. Experimental tubes were designed to allow measurements of both the transmittance and the photoemission, including the quantum-yield and energy-distribution curve, on the same surface, except for a few tubes which were intended to measure both the reflectance and the transmittance. The reflectance was measured using a conventional monochromator with a H_2-discharge lamp or a W lamp. All measurements were performed at room temperature.

III. RESULTS

A. Determination of Optical Constants

The optical constants were obtained from the KK analysis of the transmittance data for the thin film on a transparent substrate. The details of this analysis were presented in I. The thickness of the sample was estimated from the starting Sb-film thickness by multiplying by some factor which was deduced from the lattice constants of the assumed crystal structure. These factors for the compounds studied here are presented in Table I together with crystal structure, lattice constant, and the measured condictivity types. The film thickness ranged from 50 to 110 mμ. The high-energy extrapolation of the optical density in the KK analysis was estimated by fitting the calculated reflectance to the measured reflectance. The calculated reflectance is given by the known optical constants which are deduced with the appropriate high-energy extrapolation.

TABLE I. Crystal structure, lattice constant, multiplying factor to derive the film thickness from the starting Sb thickness, and conductivity type determined from the thermoelectromotive force for K_3Sb, Na_3Sb, and Na_2KSb.

Material	Crystal structure	Lattice constant (Å)	Multiplying factor	Conductivity type
K_3Sb	hexagonal	$a_0 = 6.025,$ $c_0 = 10.69^a$	6.89	n
K_3Sb	cubic	$a_0 = 8.49^b$	6.27	
Na_3Sb	hexagonal	$a_0 = 5.355,$ $c_0 = 9.496^a$	4.84	n
Na_2KSb	cubic	$a_0 = 7.724^c$	4.74	p

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[b]Reference 5.

[c]Reference 10.

B. Experimental Results

Typical transmittance curves of purple K_3Sb as a function of photon energy are shown in Fig. 1. As a comparison, Sommer's[12] curve of hexagonal K_3Sb is also presented in the figure. The peak and the dip positions of purple K_3Sb are in good agreement with those of hexagonal K_3Sb, although weak structure at photon energies above 5.0 eV is slightly different from sample to sample. From Fig. 1, it is seen that our pure purple K_3Sb is identical with K_3Sb of hexagonal structure.

Figure 2 shows the transmittance curves of two brownish-purple (Nos. 33 and 34) films and a brown (No. 44) K_3Sb film. In order to show the difference in the transmittance curves of various types of K_3Sb, the spectrum of pure purple K_3Sb is also shown. The peak positions in the second
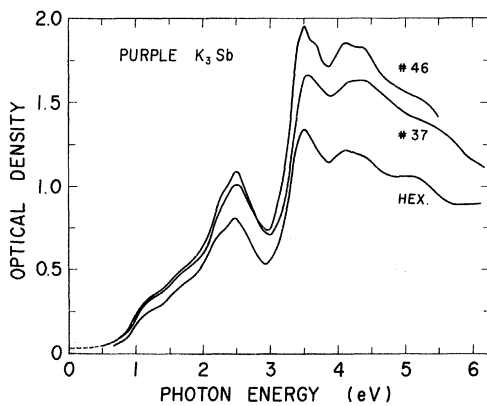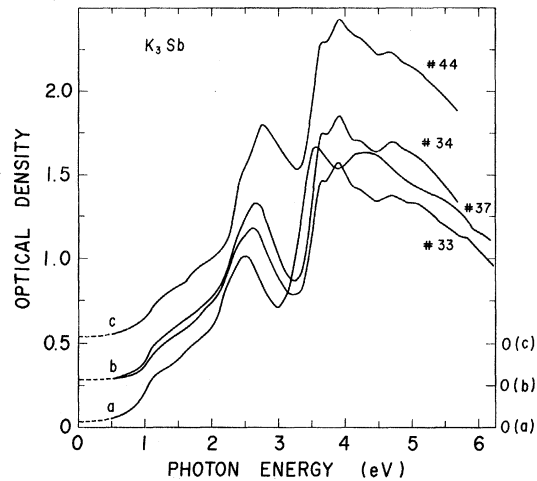

FIG. 2. Transmittance curves of brownish-purple K_3Sb (Nos. 33 and 34) and brown K_3Sb (No. 44) as a function of photon energy: No. 33, 68-mμ thickness; No. 34, 82 mμ; No. 44, 95 mμ. The transmittance curve of purple K_3Sb of No. 37 is reproduced for comparison.

strong absorption band at photon energies above 3.5 eV are very reproducible for brownish-purple K_3Sb and are in satisfactory agreement with that of a brown sample, while the peak position at about 2.6 eV in the first absorption band is different from sample to sample. The energy position of this peak seems to be sensitive to an activation condition of the films. Figure 3 shows a comparison of the transmittance curve of our brown K_3Sb with that of cubic K_3Sb of Sommer.[12] The peak positions of brown K_3Sb are in good agreement with that of cubic K_3Sb: The first peak occurs at 2.75 eV and the double peaks in the second band are at 3.65 and 3.9 eV. The dip at 3.25 eV, which is fairly pronounced for brown K_3Sb, however, does not appear for cubic K_3Sb. On the contrary, a weak peak appears instead of the dip for cubic
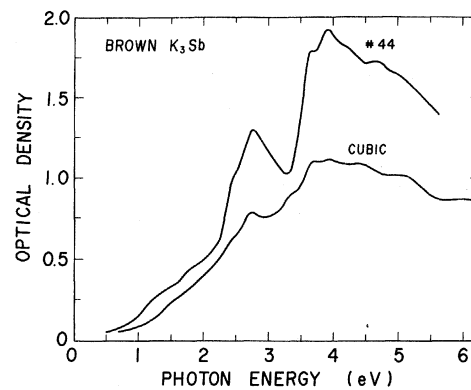

FIG. 1. Typical transmittance curves of purple K_3Sb (Nos. 37 and 46) and hexagonal K_3Sb (HEX) as a function of photon energy: No. 37, 84-mμ thickness; No. 46, 90 mμ: HEX, 66 mμ. The curve of hexagonal K_3Sb was supplied by Sommer.

FIG. 3. Comparison of the transmittance curve of our brown K_3Sb with that of cubic K_3Sb of Sommer: cubic K_3Sb (CUB), 61-mμ thickness.
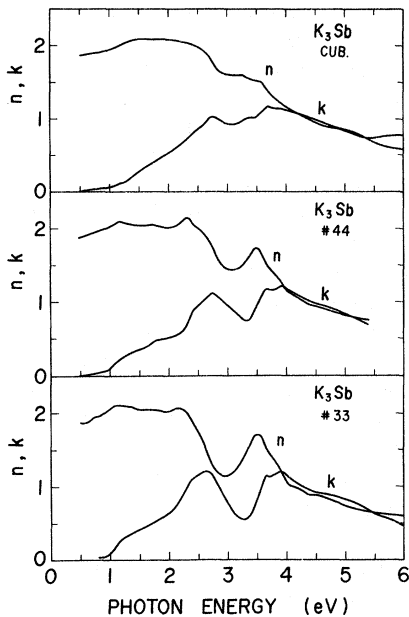
FIG. 4. Refractive index n and extinction coefficient k for brownish-purple, brown, and cubic K_3Sb from the transmittance data.

K_3Sb. As a whole, the curves of our brown K_3Sb seem to be considerably different from the curve of cubic K_3Sb. They are more similar to the curve of purple K_3Sb than to that of cubic K_3Sb. Therefore, we were unable to decide whether our brown sample is identical with K_3Sb of cubic structure.

Figure 4 shows the refractive index n and the extinction coefficient k calculated from the transmittance data for various types of K_3Sb with the omission of purple K_3Sb, which was presented in I.
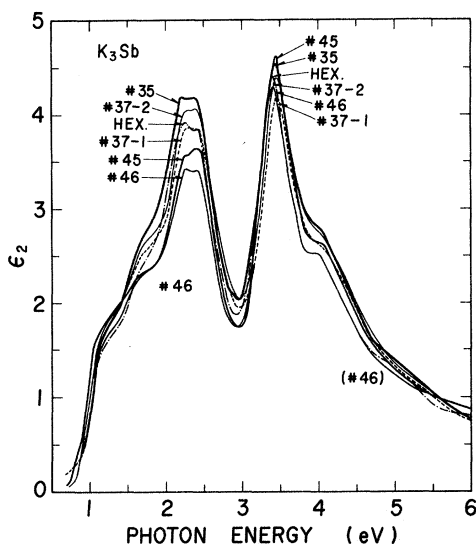
Figure 5 shows the imaginary part of the complex dielectric constant ϵ_2 as a function of photon energy for our K_3Sb and the hexagonal K_3Sb of Sommer.[12] In order to show the reliability in the preparation of the samples, examples of $\epsilon_2(\omega)$ of four K_3Sb films with various thicknesses are shown in the figure. The energy positions of the peaks in the $\epsilon_2(\omega)$ curves are in good agreement with each other, while the ratios of peak height of the first band to that of the second bands are slightly different from sample to sample. The difference in the ratios, however, is not serious. Thus this figure shows that the $\epsilon_2(\omega)$ curves of purple samples and hexagonal sample agree satisfactorily within the error of the sample thickness, which is roughly of the order of $\pm 10\%$. In order to show the effect of the thickness estimation on $\epsilon_2(\omega)$, the calculation of $\epsilon_2(\omega)$ was made for the assumed thickness of 81 mμ as well as 84 mμ in the case of sample 37. The results also are shown in the figure. These two curves indicate that the estimation of the film thickness is of importance for the determination of the absolute value of $\epsilon_2(\omega)$. This fact also is applied to n or k; for instance, n at 0.5 eV is 1.98 for 84-mμ thickness and 2.01 for 81-mμ thickness.

In Fig. 6, the curves of $\epsilon_2(\omega)$ for two brownish-purple K_3Sb films and a brown K_3Sb film are presented. The structures in the second band at high energy are in good agreement with each other from sample to sample, but the structure in the first band centered at about 2.5 eV is slightly different from sample to sample. The $\epsilon_2(\omega)$ curve of cubic K_3Sb is also presented in this figure.
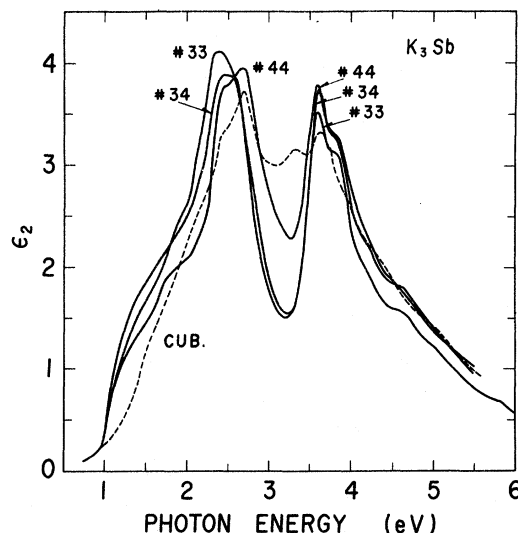
Typical transmittance curves for Na_3Sb are

FIG. 5. $\epsilon_2(\omega)$ of purple K_3Sb.

FIG. 6. $\epsilon_2(\omega)$ of brownish purple (Nos. 33 and 34) and brown K_3Sb (No. 44). $\epsilon_2(\omega)$ of cubic K_3Sb is also presented by a dashed curve.
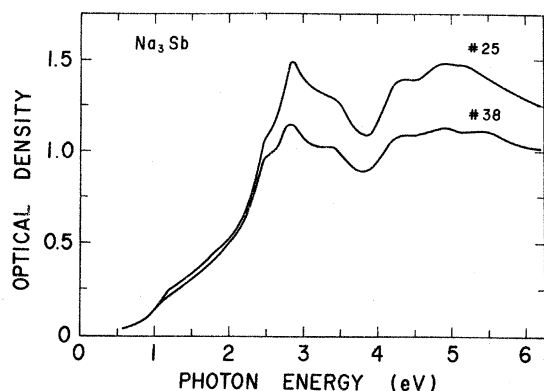
FIG. 7. Transmittance curves of Na_3Sb as a function of photon energy: No. 38, 57-mμ thickness; No. 25, 78 mμ.

shown in Fig. 7. Some structure in the spectrum is satisfactorily reproducible in its energy position. A shoulder at 2.5 eV and peaks at 2.85 and 3.4 eV in the first absorption band are well defined and reproducible, whereas the structure in the second absorption band is not marked and is reproducible only for the first peak at 4.3 eV. The other two peaks at 4.9 and about 5.3 eV are sometimes not well defined. A dip at 3.85 eV is well defined and its energy position is reproducible. The first peak at 2.85 eV and the shoulder at 2.5 eV have also been observed in Ref. 3.

Figure 8 shows the transmittance curves for one poorly photosensitive and two highly photosensitive multialkali antimonides $Na_{3-x}K_xSb$. The sensitivities of the two highly sensitive samples are slightly different from each other: Sample 23 is more sensitive to white light than sample 14. From this figure and Fig. 7, it is seen that during
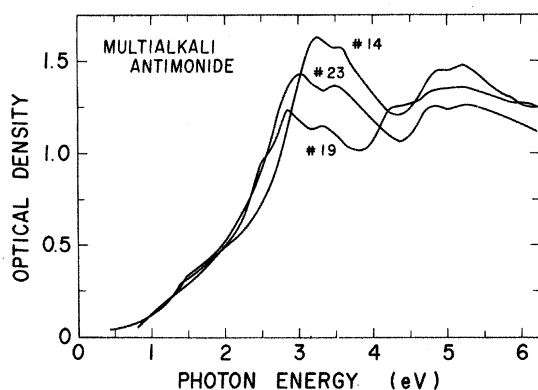
the activation process of a Na-Sb film in K vapor, the first peak at 2.85 eV and the second peak at 3.4 eV of Na_3Sb grow in absorption intensity, accompanied by an energy shift to higher energy. The spectrum of the low-sensitivity sample is almost identical with that of Na_3Sb. Both absorption bands of the high-sensitivity sample turn out to be composed of two peaks, while in Na_3Sb and the low-sensitivity sample both absorption bands are composed of three peaks. This difference in the number of peaks may be ascribed to the difference in the crystal structure: Na_3Sb is hexagonal and Na_2KSb is cubic. However, the origin of this difference can be made clear when the calculations of the energy-band structure are carried out. Of the two high-sensitivity samples, peaks in the more sensitive sample occur at 3.0 and 3.5 eV and at 4.85 and 5.25 eV. The peaks occur at 3.25 and 3.6 eV and at 4.85 and 5.25 eV in the other sample. The transmittance spectrum of the latter (sample 14) has better-defined and sharper structure than that of the most sensitive sample. The peak position of sample 14 is slightly greater than that of the S-20 photocathode,[13] which is believed to be $[Cs]Na_2KSb$.[14] The distinct difference in the transmittance curves of these two high-sensitivity samples is the energy position of the first absorption peak: The peak position of the more sensitive sample occurs at lower energy than that of the other. This difference may result in the different sensitivity to white light in these two samples, because the absorption increases at the low photon energies for the most sensitive sample. On the basis of the relation between chemical composition and photosensitivity reported in Ref. 10, sample 14, with the sharper spectrum, is believed to be the compound with composition

FIG. 8. Transmittance curves of multialkali antimonide $Na_{3-x}K_xSb$ of the poorly photosensitive sample (No. 19) and the highly photosensitive samples (Nos. 23 and 14): No. 19, 61-mμ thickness; No. 23, 71 mμ; No. 14, 59 mμ. Of the two highly photosensitive samples, No. 23 is more sensitive than No. 14.
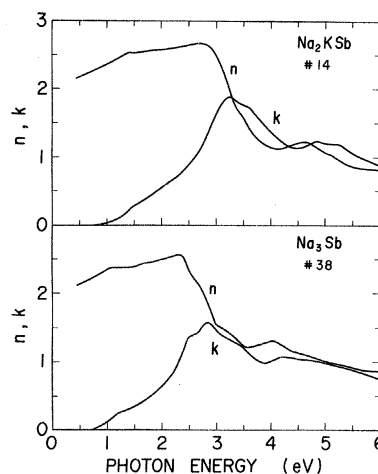

FIG. 9. Refractive index n and extinction coefficient k from the transmittance data of Na_3Sb and Na_2KSb, where sample 14 is assumed to be Na_2KSb.
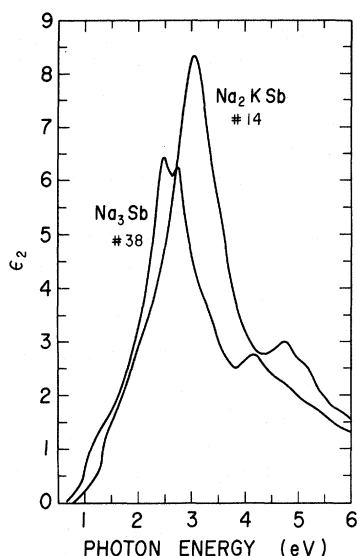
FIG. 10. $\epsilon_2(\omega)$ of Na_3Sb and Na_2KSb.

Na$_2$KSb, and sample 23, with a slightly diffuse spectrum, is believed to be the compound composed mainly of Na$_2$KSb plus a small amount of Na$_3$Sb. Alternatively, the difference in the two spectra may be attributed not to the difference in the chemical composition but to the state of crystallization, i.e., the amorphous and crystalline state of Na$_2$KSb. We assume, however, that sample 14 is Na$_2$KSb.

The optical constants n and k calculated from the transmittance data using the KK dispersion relations are shown in Fig. 9 for Na$_3$Sb and Na$_2$KSb. Figure 10 shows the curves of $\epsilon_2(\omega)$ for these compounds. The high-energy extrapolation was given using a fitting of the calculated reflectivity to the measured reflectance data. For sample 14, the optical density was assumed to be constant from 6.2 to 8.0 eV and then to decrease linearly with photon energy to zero at 20.0 eV. The calculated reflectivity using this assumption was in satisfactory agreement with the measured reflectivity. For Na$_3$Sb, the optical density was assumed to be constant from 6.2 to 11.0 eV and to decrease to zero at 16.0 eV.

The peak positions in the absorption spectra of K$_3$Sb, Na$_3$Sb, and Na$_2$KSb as a function of alkali-metal composition are summarized in Fig. 11. As mentioned above, the composition of the most photosensitive sample is assumed to be Na$_2$KSb plus Na$_3$Sb. The peak position of this sample is shown not by the point but by the short line in this figure, because the molar compositions of K and Na are undetermined. In connection with the variation of the band gaps with component composition in the semiconductor-alloy systems, it has been reported that the energy gaps of the pseudo-

binary system vary as a quadratic function of component composition.[15,16] We assume a linear variation of the peak position with component composition for the K$_3$Sb-Na$_2$KSb-Na$_3$Sb system. The tentatively assumed changes of the peak positions are shown in Fig. 11 as the solid and the dotted lines. These results are of importance for future consideration of the electronic structure of alkali-antimony compounds.

The refractive index at 0.5 eV and the square root of the effective dielectric constant, $\epsilon_{eff}(\omega)^{1/2}$, integrated up to 10.0 eV, are summarized in Table II for the compounds studied in the present work, where $\epsilon_{eff}(\omega)$ was evaluated, as usual, by the KK analysis of the real part of the complex dielectric constant. Table II shows that $\epsilon_{eff}(\omega)^{1/2}$ approaches a value n at 0.5 eV as expected, where 0.5 eV is considered to be low enough compared with the lowest band gap.

IV. DISCUSSION

According to the earlier report,[3] the lowest band gap of alkali antimonides does not appear to vary appreciably with component alkali metal except in the case of Cs$_3$Sb. The lowest band gaps of K$_3$Sb of hexagonal structure and Na$_3$Sb and of Na$_{3-x}$K$_x$Sb have been estimated to be about 1.1 and 1.0 eV, respectively, as derived from the photo-conductivity response.[3] Measured transmittance curves for these compounds are very similar in
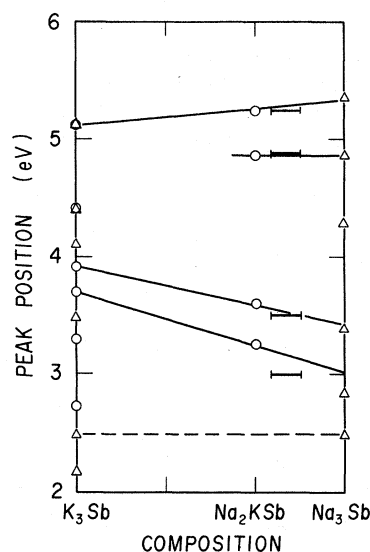

FIG. 11. Peak positions in the optical density as a function of alkali-metal composition for K$_3$Sb, Na$_3$Sb, and Na$_2$KSb: Circles are for cubic compounds and triangles for hexagonal compounds. The short lines show the peak positions for sample 23, where it is assumed to be Na$_2$KSb + Na$_3$Sb. The variation of the peak position with alkali-metal composition·is tentatively assumed by the solid and dotted lines.

TABLE II. Refractive index n at 0.5 eV and square root of effective dielectric constant, $\epsilon_{eff}(\omega)^{1/2}$, integrated up to 10.0 eV for the samples studied here.

Material	Sample No.	Thickness (mμ)	n at 0.5 eV	$\epsilon_{eff}(\omega)^{1/2}$
K$_3$Sb (hexagonal)	37	84	1.98	1.98
		81	2.01	2.01
	35	72	2.01	2.02
	45	109	(1.85)	2.00
	46	90	1.99	2.01
	HEX	66	1.95	1.97
K$_3$Sb (cubic)	CUB	61	1.85	1.89
K$_3$Sb (brownish purple)	33	68	1.88	1.89
	34	82	1.89	1.99
K$_3$Sb (brown)	44	95	1.88	1.90
Na$_3$Sb	38	57	2.12	2.14
	25	78	1.99	2.05
Na$_2$KSb	14	59	2.16	2.19

the photon energies near 1.0 eV, as can be seen in Figs. 1, 7, and 8. In contrast to this similarity, the transmittance curves of these compounds at photon energies above the fundamental absorption edge are markedly different. These spectra are also different from that of Cs$_3$Sb[4] or K$_2$CsSb.[17] The spectrum of Cs$_3$Sb is somewhat similar to that of K$_2$CsSb. For the case of K$_3$Sb the $\epsilon_2(\omega)$ curves of both the hexagonal and the cubic structure consist of two bands of nearly equal intensity. On the other hand, the $\epsilon_2(\omega)$ curves of Na$_3$Sb and Na$_2$KSb consist of one band followed by a weak second band of higher energy. The intensity ratio of these two bands for K$_3$Sb is very different from that of Na$_3$Sb or Na$_2$KSb. In the case of semiconductors[18] of zinc-blende type including the group-IV elements and the III-V or II-VI compounds, the $\epsilon_2(\omega)$ curves are fairly similar in the gross shape, except for the shift of the energy positions. The pronounced structure at photon energies up to some 6 eV is composed of two bands: The first band at lower energy is caused by the transitions from the upper valence level to the lowest conduction level at the near L and Λ points, and the second is related to the transitions caused mainly at such points as X, Δ, Σ, and K. Generally, the intensity of the second band is greater than that of the first in the zinc-blende-type semiconductors. On the high-energy side of the second band, a somewhat weak band related to the transitions to the second-lowest level in the conduction band near the L point is observed. In brief, the $\epsilon_2(\omega)$ curves of these numerous semiconductors are very similar in the gross shape, and this fact may be ascribed to the symmetry of the crystal structure. The same similarity has also been reported for the compounds of antifluoride structure such as

Mg$_2$Si, Mg$_2$Ge, and Mg$_2$Sn.[19,20] The spectrum of these compounds consists of a main peak caused by X, Δ, Σ, and K transitions and weak peaks of both lower and higher energy than the main peak which are caused by both L and Λ transitions. Although the relative intensities of the main peak, the lowest L, and the second-lowest L transitions are different between the zinc-blende-type and antifluoride-type semiconductors, the transitions at the singularity points near L and X contribute mainly to the structure in $\epsilon_2(\omega)$.

Despite many theoretical calculations of the energy-band structure of typical semiconductors,[18,21] no theoretical calculation is available for the alkali-antimony compounds. Thus it is impossible to identify the measured structure in $\epsilon_2(\omega)$. However, possible identifications of the peaks are made on the basis of the crystal structure of the cubic alkali-antimony compounds. The sublattice of Sb and three sublattices of alkali atoms are all fcc: Three alkali atoms are arranged on a cubic diagonal of the Sb lattice at equal intervals. If the Sb lattice and only one alkali-atom lattice of the two equivalent lattices of which atoms are the nearest neighbors of the Sb atom are taken into account, the zinc-blende structure results. If the Sb lattice and these two alkali-atom lattices are taken into account, the cubic-antifluoride structure is obtained. The actual crystal structure of cubic alkali-antimony compounds is composed of the antifluoride lattice plus the alkali-atom lattice composed of the atoms at the cube center of the antifluoride lattice. The $\epsilon_2(\omega)$ curves of Na$_3$Sb and Na$_2$KSb are fairly similar to those of the antifluoride compounds in their gross shape. On the basis of this similarity, the main peak in $\epsilon_2(\omega)$ for Na$_3$Sb and Na$_2$KSb may be caused mainly by the X transitions including Δ and Σ transitions, and the second weak peak on the high-energy side of the main peak may come mainly from the L and Λ transitions. The steep rise in $\epsilon_2(\omega)$ at 1.0 and 1.3 eV for Na$_3$Sb and Na$_2$KSb, respectively, may be related to the lowest direct transitions. The value of 1.3 eV for the direct lowest band gap in Na$_2$KSb is somewhat greater than the previously reported value of 1.0 eV derived from the photoconductivity response.[3] The absorption intensities below 1.3 eV are certainly too great if Na$_2$KSb is a direct-gap semiconductor. Thus these absorptions may be ascribed to the indirect transitions, which result in the photoconductivity response at the photon energies below 1.3 eV. In fact, the antifluoride compounds such as Mg$_2$Si have been reported to be indirect-gap semiconductors,[20] and in an earlier investigation a band model with indirect gap has been proposed for Cs$_3$Sb.[22]

The $\epsilon_2(\omega)$ curve for cubic K$_3$Sb consists of two bands with nearly equal intensity. This curve is

more similar to the curve of typical zinc-blende-type compounds than to that of antifluoride compounds. The low-energy bands may be caused by the transitions at the L and Λ points and the high-energy band at the X, Δ, and Σ points.

According to the studies on the spin-orbit splittings in the zinc-blende-type compounds,[23] the splitting of the upper valence-band level of the III-V compounds containing Sb is some 0.8 eV at the Γ point, and at the L point it is about $\frac{2}{3}$ of the value at the Γ point. These splittings are mainly caused by the splitting of the anion constituent. The splitting of the upper valence level at the X point is influenced by both the anion and cation constituents. The spin-orbit splittings of the alkali atoms Na and K are believed to be fairly small compared with that of the Sb atom. Thus in the present case both the splittings at the L and X points are expected to be of the order of 0.5 eV. The peak at 2.7 eV and the shoulder at near 2.4 eV in $\epsilon_2(\omega)$ for cubic K_3Sb may be caused by the spin-orbit splitting. The two peaks at 3.6 and 3.75 eV in $\epsilon_2(\omega)$ may or may not be related to the spin-orbit splitting, because the energy difference of 0.15 eV is somewhat smaller than the expected value of some 0.5 eV, whereas the doublet structure at 4.6 and 5.0 eV may be related to the spin-orbit splitting. For the case of hexagonal K_3Sb,

the low-energy peak at 2.3 eV and the shoulder at about 1.6 eV as well as the high-energy peak at 3.45 eV and the shoulder at 4.0 eV may all be caused by the spin-orbit splittings. In the case of Na_3Sb, some peaks making up the structure in the two bands of the transmittance curve (see Fig. 7) may be related to the spin-orbit splittings. For Na_2KSb, the observed doublet structure of the two bands in the transmittance curve (see Fig. 8) may also be attributed to the spin-orbit splitting: The splitting of the first band is about 0.35 eV and that of the second is about 0.4 eV. Although the measured splittings in the $\epsilon_2(\omega)$ or the transmittance curves for the compounds studied in the present work are nearly in agreement with the expected values for the spin-orbit splitting, the identifications of the estimated spin-orbit splittings should be verified when the energy-band structures for alkali-antimony compounds become available.

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