Energy Gap in β -Ag₂Se[†]

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The energy gap of the modification of silver selenide stable below 133°C has been investigated. Studies of the optical-absorption spectrum at 80°K and at 5°K and of the temperature variation of the Hall coefficient and electrical conductivity have been made on polycrystalline samples. Analysis of the data on the electrical properties in the intrinsic region suggests the existence of two phases, not distinguishable by x-ray diffraction, with energy gaps E_0 at 0°K of 0.07 ± 0.01 eV and 0.18 ± 0.01 eV, respectively. The latter value agrees with that proposed for the β_2 phase of β -Ag₂Se reported by Baer. The optical-absorption spectra suggest that the band-to-band transitions observed are direct. The extrapolated threshold of absorption is at 0.13 eV at 5°K and correlates best, because of the probable Burstein shift of the absorption edge, with the proposed value of $E_0 = 0.07$ eV. It is also concluded that the energy gap increases as the temperature decreases.

I. INTRODUCTION

HE low-temperature (β) polymorph of silver selenide, stable below 133°C, is one of the small number of semiconductors reported to have an energy gap E_0 at 0°K of less than 0.1 eV. As such, it is of considerable interest. Junod has reported values of E_0 of 0.075 eV1 and of 0.07 eV.2 Akhundov et al.3 have proposed an activation energy (at an unspecified temperature) of 0.09 eV using data on the electrical conductivity. Simon et al.⁴ propose a value of the energy gap of approximately 0.03 eV at room temperature. There exists some uncertainty in the literature concerning the structure of the low-temperature phase. Earley⁵ did not describe the unit cell, but determined a set of d values. Boettcher et al.,6 working with films 500 Å thick, report four tetragonal phases below 133°C. Baer et al.⁷ propose the existence of two low-temperature phases, β_1 and β_2 , with a transition temperature of 90°C. These workers give no lattice parameters, but it appears that their β_1 phase is the same as the tetragonal phase reported by by Boettcher as having a = 7.06 Å and c = 4.98 Å. Baer et al. report that x-ray powder photographs show the same d values for the β_1 and β_2 modifications and that the intensities were different. They suggest that the two phases have different atomic ordering and propose values of $E_0 = 0.05$ eV for the β_1 phase and $E_0 = 0.18$ eV for the β_2 phase. Simon *et al.*⁴ report that the low-temperature phase is orthorhombic with $a_0 = 7.044$ Å, $b_0 = 7.748$ Å, and $c_0 = 4.328$ Å.

As part of a study of I-VI compound semiconductors, the Hall coefficient R and electrical conductivity σ of

⁷Y. Baer, G. Busch, C. Frolich, and E. Steigmeier, Z. Naturforsch. **17a**, 886 (1962).

this material have been studied as a function of temperature. To complement the study of the electrical properties, the optical-absorption spectrum of evaporated films of silver selenide has been measured at 80°K and 5°K. The analysis of the results has provided information on the value of the energy gap at 0°K and on the existence of the β_2 phase.

II. EXPERIMENTAL

The polycrystalline ingots of silver selenide were prepared by reaction of the elements in the liquid state. Silver (American Smelting and Refining Co. grade A-59, quoted purity 99.999+%) and selenium (American Smelting and Refining Co. grade A-58, quoted purity 99.999+%) were placed in an ampoule evacuated to a pressure of about 10⁻⁵ Torr. Two methods were used to freeze the liquid mixture. The first was the use of a Bridgman-type two-zone (800°C and 900°C) furnace in which the reactant mixture was passed through a freezing plane. This method was used to prepare sample AS-1. The second, simpler arrangement held the liquid at about 1000°C for several hours; the mixture was then cooled slowly. This method was used for the preparation of samples AS-2, AS-4, and AS-5. All ingots except AS-4 were nominally stoichiometric; ingot AS-4 contained 0.37 atomic% excess selenium. Neither method produced single-crystal ingots. Presumably this was due to the phase transformation at 133°C and parallels our experience with β -Ag₂Te.

Portions of all four polycrystalline ingots were examined by x-ray diffraction using powder patterns and diffractometry. The patterns at room temperature were identical, showed no discernable differences in relative intensities and agreed with the data reported by Earley.⁵ In addition, study⁸ of several samples by high-temperature diffractometry and high-temperature powder photographs showed no differences in patterns or intensities which would indicate the existence of a second phase. It should be noted that, because of the nature of photographic intensity data, a mixture of two phases (i.e., β_1 and β_2) could be present and not be

⁸ R. Dalven, W. H. McCarroll, and R. J. Paff (unpublished).

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¹ P. Junod, Helv. Phys. Acta **30**, 470 (1957). ² P. Junod, Helv. Phys. Acta **32**, 567 (1959).

³ G. A. Akhundov et al., in Proceedings of the Fourth All-Union Conference on Semiconductor Materials, edited by N. X. Abrikosov (Consultants Bureau Special Research Report, New York, 1963). ⁴ R. Simon, R. C. Bourke, and E. H. Lougher, Advan. Energy Conversion 3, 481 (1963).

⁵ J. Earley, Am. Mineralogist **35**, 337 (1950). ⁶ A. Boettcher *et al.*, Z. Angew. Physik **7**, 478 (1955).



FIG. 1. Sample configuration and apparatus.

discernable. Differential thermal analysis⁸ of two samples (portions of ingots AS-2 and AS-5) showed no sign of a phase transition between 20 and 133°C.

Since we were unable to prepare single crystals of silver selenide, all measurements were made on polycrystalline samples. The ingots were etched with aqueous HF and then with a mixture of $NH_3 + H_2O_2$. Discs were then prepared and polished to a thickness of approximately 0.1 cm. After further etching to remove a surface layer, six-arm bridge-type samples were prepared by ultrasonic cutting. The configuration is shown in Fig. 1; the ratio of length to width (5.2) satisfied the criterion given by Dunlap⁹ for avoiding spuriously low values of the Hall coefficient. Soldered contacts, described in detail elsewhere, ¹⁰ were used and DC measurements of Hall coefficient R and electrical conductivity σ were made using standard methods. A block diagram of the apparatus is shown in Fig. 1 as is the numbering system used for contacts. Thus R_{26} is a value of the Hall coefficient determined from voltages measured between contacts 2 and 6. For measurements above room temperature, the sample was heated with a high-intensity lamp. The sample was in a brass can filled with helium during all measurements. Conventional thermometric and cryogenic techniques were used; the temperatures reported are estimated to be accurate to $\pm 1^{\circ}$ K. In the standard manner,¹¹ the directions of both the sample current and of the magnetic field were reversed to eliminate errors due to probe misalignment, thermoelectric effects, etc. It was necessary to make two runs over a given temperature range to obtain data for both directions of the magnetic field. Each Hall voltage used was the arithmetic mean of the appropriate four values of the measured voltage. A magnetic intensity of 5000 G was used.

The samples for optical-absorption measurements were thin polycrystalline films prepared by the evaporation in vacuum of silver selenide (from ingot AS-1) at about 1500°C onto single-crystal KBr substrates. The film thicknesses were 6×10^{-5} and 2×10^{-4} cm. The x-ray powder patterns of the evaporated layers were identical to that of the starting material except that one contained a few atomic percent of silver. The conventional "sample-in, sample-out" method was used to determine the transmission spectrum of each sample. A Leiss double-prism monochromator was the dispersing element of the single-beam recording spectrophotometer used and phase-sensitive detection was employed. The relation $T = F(R) \exp(-\alpha \tau)$ was used, where T is the transmissivity, F(R) is a function of the reflectivity R, τ is the sample thickness, and α is the absorption coefficient. The absorption spectrum at 80°K and 5°K was determined from 0.09 eV to about 0.6 eV using the transmission spectra of the two samples of different thickness.

III. RESULTS AND DISCUSSION

From the four ingots of silver selenide synthesized (AS-1, AS-2, AS-4, AS-5), a total of five samples were prepared for measurement of Hall coefficient and conductivity. All samples were found to be *n* type to 4.2°K. Typical data on the Hall coefficient *R* are shown in Fig. 2; *R* was measured at two points (R_{26} and R_{35}) on each sample. The conductivity σ was also determined at two points on each sample (σ_{23} and σ_{56}). These data on the temperature variation of *R* and σ were used to study the value of the energy gap in β -Ag₂Se. For a nondegenerate intrinsic semiconductor with parabolic bands and a linear variation $\Delta E = E_0 + \alpha T$ of the energy gap ΔE with temperature, a plot of $\ln |R| T^{3/2}$ versus (1/T) will be linear with a slope $(E_0/2k)$. Here E_0 is the value



FIG. 2. Hall coefficient $|R_{26}|$ versus (1/T) for sample AS-5-1.

⁹ W. C. Dunlap, An Introduction to Semiconductors (John Wiley & Sons, Inc., New York, 1957), pp. 185–187.

¹⁰ R. Dalven and R. Gill, Phys. Rev. 143, 666 (1966).

¹¹ E. H. Putley, *The Hall Effect and Related Phenomena* (Butterworths Scientific Publications, Ltd., London, 1960), pp. 42-43.

TABLE I. Slopes S_1 of plots of $\ln |R| T^{3/2}$ and S_2 of $\ln \sigma$ versus (1/T) for samples AS-1-1, AS-1-2, and AS-4-7. The quantity k is Boltzmann's constant.

Sample	Run	Data	$2kS_1$ (eV)	Data	$-2kS_2$ (eV)
AS-1-1	1	R_{26}	0.042	σ23	0.045
	1	R_{35}	0.043	σ56	0.056
	2	R_{26}	0.039	σ22	0.046
	2	R_{35}	0.035	σ56	0.062
	3	R_{26}	0.041	- 00 Π 99	0.047
	3	R_{35}	0.044	- 20 στε	0.066
	4	R_{26}	0.039	- 00 Π 99	0.049
	4	R_{35}	0.037	σ_{56}	0.062
AS-1-2	1	R_{26}	0.048	σ_{23}	0.085
	1	R_{35}		σ56	0.077
	2	R_{26}	0.033	σ23	0.083
	2	R_{35}	0.029	0 56	0.077
	3	R_{26}	0.033	0 93	0.084
	3	R_{35}^{20}	0.025	σ_{56}	0.078
AS-4-7	1	R_{26}	0.029	G 93	0.083
	1	R_{35}^{20}	0.023	σ_{56}	0.070
	A	verage	(0.036		(0.067
			±0.006) eV		± 0.013) eV

of ΔE at 0°K and k is Boltzmann's constant. If, in addition, the carrier mobility varies as $T^{-3/2}$, a plot of $\ln \sigma$ versus (1/T) will be linear with a slope $(-E_0/2k)$. In Tables I and II are shown the slope S_1 of the several plots of $\ln |R| T^{3/2}$ versus (1/T) and the slope S_2 of the plots of $\ln \sigma$ versus (1/T). The quantity k is Boltzmann's constant. Representative data are shown in Figs. 3 and 4.

On examining the data in Tables I and II it is seen that the results are quite different for the two groups of samples. From Table I, the average value of $(2kS_1)$ is (0.036 ± 0.006) eV and that of $(-2kS_2)$ is (0.067 ± 0.013) eV. We identify the quantities $(2kS_1)$ and $(-2kS_2)$ with E_0 by assuming nondegeneracy, a $T^{-3/2}$ mobility variation, etc. as discussed above. For this trio of specimens then there are essentially two values of E_0 from which to choose. In general,¹² conductivity mea-



FIG. 3. Plot of $\ln |R_{26}| T^{3/2}$ versus (1/T) for sample AS-1-1.

¹² R. A. Smith, *Semiconductors* (Cambridge University Press, London, 1961), p. 330.



FIG. 4. Plot of $\ln \sigma_{23}$ versus (1/T) for sample AS-5-1.

surements on polycrystalline samples may be unreliable and not truly representative of bulk material because of intercrystallite barrier resistance. Hall coefficient data are often thought to be more desirable in such cases. However, in this instance the conductivity data seem to be preferable because (1) the scatter of experimental points is greater for plots of $\ln |R| T^{3/2}$ versus (1/T) and (2) there is some evidence that the region in which the mobility varies as $T^{-3/2}$ extends to lower temperatures in Ag₂Se than in Ag₂Te.¹³ For these reasons, the value (0.067 ± 0.013) eV is suggested as more reliable. In view of the data, no correction for the probable degeneracy of the semiconductor was made. A value of $E_0 = (0.07)$ ± 0.01) eV is therefore proposed for the energy gap at 0°K for samples AS-1-1, AS-1-2, and AS-4-7. The average values of $(2kS_1)$ and $(-2kS_2)$ for the samples listed in Table II show a choice similar to that in Table I. Again, for the same reasons as described above. we suggest that the value of E_0 derived from conductivity data is more reliable. Accordingly, it is proposed that samples AS-2-2 and AS-5-1 are best characterized

TABLE II. Slopes S_1 of plots of $\ln |R| T^{3/2}$ and S_2 of $\ln \sigma$ versus (1/T) for samples AS-2-2 and AS-5-1. The quantity k is Boltzmann's constant.

Sample	Run	Data	$2kS_1$ (eV)	Data	$-2kS_2$ (eV)
AS-2-2	1 1 2 2 3 3	$R_{26} \ R_{35} \ R_{26} \ R_{35} \ R_{26} \ R_{35} \ R_{26} \ R_{35} \ R_{26} \ R_{35} \ R_{35}$	0.196 0.058 0.145 0.108 0.136 0.079	$\sigma_{23} \\ \sigma_{56} \\ \sigma_{23} \\ \sigma_{56} \\ \sigma_{23} \\ \sigma_{56} \\ \sigma_{56}$	0.182 0.177 0.159 0.162 0.177 0.162
AS-5-1	1 1	$egin{array}{c} R_{26} \ R_{35} \ Average \end{array}$	$0.085 \\ 0.131 \\ (0.117 \\ \pm 0.035) \text{ eV}$	$\sigma_{23} \\ \sigma_{56}$	0.206 0.176 (0.175 ± 0.011) eV

¹³ R. Dalven and R. Gill, J. Appl. Phys. (to be published).



FIG. 5. Optical-absorption spectrum of β -Ag₂Se at 80°K and 5°K.

by a value of $E_0 = (0.18 \pm 0.01)$ eV. This figure may be compared with the value of 0.18 eV reported by Baer *et al.*⁷ for their β_2 phase.

To supplement the study of the electrical properties, the optical-absorption spectrum of evaporated films of silver selenide was measured at 80°K and at 5°K. Figure 5 shows these results, which are the first absorption spectra reported for β -Ag₂Se. Both spectra show the shape characteristic of the absorption of a semiconductor in the region of the fundamental absorption edge. The sharp increase in absorption coefficient α beginning at about 0.15 eV is believed to be due to transitions from the valence band to the conduction band. This increasing absorption continues to a photon energy of 0.35 eV in the case of the spectrum at 5° K and to higher photon energies in the 80°K spectrum. In both cases this increasing absorption is believed to be the fundamental absorption edge. The increase in absorption at photon energies below about 0.15 eV is due to absorption by free carriers. It may be noted that the free-carrier absorption is smaller at 5°K than at 80°K.

It is pertinent to use these data to determine a value of the optical energy gap at 0°K. To accomplish this, it is necessary to extrapolate the band-to-band absorption to zero absorption coefficient. Even though the fundamental absorption edge at 5°K is reasonably steep, a more reliable method of extrapolation is desirable. It is known¹⁴ that the functional variation of the absorption coefficient α with photon energy will depend on the nature of the transition in question. For a parabolic band model, $\alpha^n = A (h\nu - E_g)$, where n = 2 or $\frac{2}{3}$ for direct transitions, $n = \frac{1}{2}$ or $\frac{1}{3}$ for indirect transitions, $h\nu$ is the photon energy, and E_{σ} is the energy gap. These powers of α have been plotted as a function of $h\nu$ and it was found that the plot of α^2 versus $h\nu$ gave the best straight line. This plot is shown in Fig. 6 for 80°K and for 5°K. The intercept of the extrapolation to $\alpha=0$ of both straight lines is approximately 0.13 eV. The linearity of these plots supports the belief that the fundamental absorption edge is being observed.

If, as is suggested by the linearity of the plot of α^2 versus $h\nu$, the optical transitions are direct, then the optical and thermal energy gaps are the same at a given temperature. We may therefore compare these optical results directly with the results of the study of the electrical properties. The existence of a Burstein shift of the absorption threshold to higher photon energies is to be expected for small energy-gap semiconductors. Such a shift has been reported¹⁵ in β -Ag₂Te at 300°K. Hence, the observed value of the intercept is probably the sum of the optical energy gap and a Burstein shift. Thus, the optical energy gap of the silver selenide in these optical samples will be somewhat less (a reasonable estimate, by analogy with β -Ag₂Te,¹⁵ is a few hundreths of an electron volt) than 0.13 eV. It is therefore suggested that these absorption spectra correlate best with the value of $E_0 = 0.07$ eV that has been proposed. The optical data provide no information regarding the β_2 phase.

The following conclusion may also be drawn from the optical data. It is noted from Fig. 5 that the freecarrier absorption decreases on cooling from 80°K to 5°K. Assuming that this is due to a decrease in the number of free carriers, the magnitude E_B of any Burstein shift would also decrease on cooling. Since the intercept (assumed to be the sum of E_B and the optical energy gap) is the same at 5°K and at 80°K, it may be concluded that the energy gap of β -Ag₂Se



¹⁵ R. Dalven, Phys. Rev. Letters 16, 311 (1966).

¹⁴ See, for example, R. A. Smith, *Wave Mechanics of Crystalline Solids* (John Wiley & Sons, Inc., New York, 1961), Chap. 13.

increases on cooling. This behavior is the case for most semiconductors.

IV. SUMMARY AND CONCLUSIONS

The electrical properties of several polycrystalline samples of β -Ag₂Se with identical x-ray diffraction patterns have been studied as a function of temperature. The results suggest the existence of two phases with energy gaps at 0°K of 0.07 eV and 0.18 eV, respectively. The latter value agrees with the figure reported by Baer et al.⁷ for the β_2 phase. The threshold of optical absorption due to direct band-to-band transitions was 0.13 eV at 5°K. The probable existence of a Burstein shift of the absorption edge suggests that these optical data correlate best with the value of $E_0 = 0.07$ eV. The optical-absorption data also indicate that the energy increases on cooling.

It appears that further study of the energy gap of β -Ag₂Se is warranted. It would be of primary importance to make measurements of the temperature variation of the electrical properties on well-defined singlecrystal samples if they can be prepared. Such studies would certainly be of great assistance in defining the semiconductor properties of β -Ag₂Se in general, and in providing further information on the β_2 phase in particular.

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Exciton-Donor Complexes in Semiconductors*

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The binding energy of an exciton bound to a neutral donor is estimated using the quantum-mechanical variational principle. We obtain the dissociation energy of an exciton-donor complex as a function of the ratio of the effective mass of the electron to that of the hole. The theoretical analysis is carried out within the framework of the effective-mass approximation, assuming a simple model of a semiconductor with parabolic energy bands.

I. INTRODUCTION

CONSIDERABLE amount of optical data in semiconductors can be interpreted as resulting from the existence of excitons bound to impurity centers in semiconductors. Haynes¹ studied the photoluminescence of Si of known donor and acceptor concentrations and interpreted the observed spectral lines as resulting from complexes involving an exciton associated with a neutral donor or with a neutral acceptor. From his results one finds that the dissociation energy of the exciton-neutral-donor complex is nearly 0.13 times the ionization energy of the donor. This ratio is independent of the chemical nature of the impurity atoms (Sb,P,As,Bi). Several authors²⁻⁶ also observed similar spectra in the photoluminescence of defect-exciton

complexes in II-VI compounds, namely ZnS, CdS, ZnSe, and CdTe. They find the ratio of the dissociation energy⁷ of the complex to the ionization energy of the donors to be about 0.20. No detailed theoretical calculations of the binding energy of the ground states of such complexes have yet been reported. The object of the present work is to attempt an investigation of this subject. We have assumed that the effective-mass approximation is valid and that the constant energy surfaces are spherical. Making use of a method due to James and Coolidge⁸ for the calculation of energy matrix elements, we have obtained the ratio of the dissociation energy of the exciton-neutral-donor complex to the ionization energy of the neutral donor as a function of σ , the ratio of effective mass m_e of the electron to the effective mass m_h of the hole. Our calculations of these energy ratios for the cases of Si and CdS yield the values 0.13 and 0.125, respectively, which compare not too unfavorably with the corresponding experimental results, namely 0.13 and 0.20. The next section is

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^b Y. S. Park, C. W. Litton, T. S. Collins, and D. C. Reynolds, Phys. Rev. 143, 512 (1966).
⁶ W. J. Choyke, D. P. Hamilton, and Lyle Patrick, Phys. Rev.

W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. 133, A1163 (1964)

⁷ The dissociation energy of a donor-exciton complex is the energy absorbed when the complex dissociates into a neutral donor and a free exciton.

⁸ H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933),