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Fundamental Optical Absorption in the IIA-VIB Compounds[*]

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The fundamental optical absorption in the range of $h\nu$ from 2.5 to 5.8 ev has been measured on well-annealed thin films of the following compounds: BaO, SrO, BaS, SrS, CaS, BaSe, SrSe, CaSe, MgSe, BaTe, SrTe, CaTe, and MgTe. The absorption peaks are ascribed to excitons and are observed to shift to lower energies for increasing atomic numbers of either the IIA or VIB elements. A doublet splitting is observed which is close to the values for the spin-orbit splitting of the free negative VIB ions for the selenides and tellurides but which is somewhat larger for the heavier oxides and sulfides.

INTRODUCTION

The IIA-VIB compounds, that is the oxides, sulfides, selenides, and tellurides of the alkaline earth metals, may be regarded as the divalent counterparts of the alkali halides, the IA-VIIB compounds. Most of the compounds of both of these groups have the same cubic crystal structure,[1] and all are made up of ions having closed-shell electronic configurations similar to those of the rare gases. As a result of this basic simplicity and regularity of structure, the alkali halides have long proved useful for testing various theories pertaining to ionic solids.[2] From this point of view, comparable data for the IIA-VIB compounds would be very desirable. However, except possibly for the oxides, there has been very little information published on these materials. In the present investigation we have carried out a preliminary survey of the fundamental optical absorption for thirteen of the sixteen IIA-VIB compounds. As data for MgO have been reported previously, only CaO and MgS remain to be investigated.

Most of the previous work on the fundamental optical absorption of the IIA-VIB compounds has been on the oxides. Okumura[3] and Zollweg[4] investigated the absorption in thin films of BaO and Jahoda[5] obtained similar results by analyzing the reflectance from single crystals. Measurements on thin films of SrO have been reported by Sproull.[6] The reflectance from single crystals of MgO has been measured by Nelson[7] and by Reiling and Hensley[8] who also made absorption measurements using thin films. Cheroff, Okrasinski, and Keller[9] obtained qualitative results on the fundamental absorption edge in single crystals of SrS. Since the completion of the present investigation, a paper by Zollweg[10] has appeared on the fundamental optical absorption and photoemission for the oxides, sulfides, selenides, and tellurides of barium and strontium. Since Zollweg has duplicated about half of the new results to be reported here and since we are in essential agreement with his conclusions, our results will be given in greatly condensed form.

EXPERIMENTAL PROCEDURE

The optical absorption measurements were made with a single-pass, double-beam, quartz prism, spectrophotometer similar to Perkin-Elmer's Model 13. A low-pressure hydrogen arc was used as a radiation source, and an RCA 1P28 photomultiplier tube was used as a detector. The resolution was better than 0.005 ev over most of the spectral range covered.

The samples were prepared and measurements made in tubes of the type indicated in Fig. 1. The thin-film

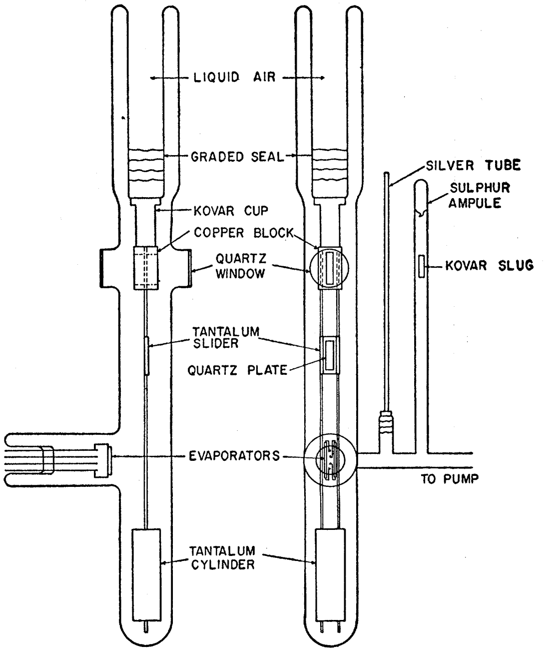

Fig. 1. Construction of optical absorption tube.

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[1] All have NaCl structure except CsCl, CsBr, and CsI which have CsCl structure and MgTe which has a wurtzite structure. Mg is included here as a IIA element; however, Be is not.

[2] F. Seitz, Revs. Modern Phys. **18**, 384 (1946); **26**, 7 (1954).

[3] Koji Okumura, Phys. Rev. **96**, 1704 (1954).

[4] R. J. Zollweg, Phys. Rev. **97**, 288 (1955).

[5] F. C. Jahoda, Phys. Rev. **107**, 1261 (1957).

[6] R. L. Sproull, Phys. Rev. **78**, 630 (1950).

[7] J. R. Nelson, Phys. Rev. **99**, 1902 (1955).

[8] G. H. Reiling and E. B. Hensley, Phys. Rev. **112**, 1106 (1958).

[9] Cheroff, Okrasinski, and Keller, J. Chem. Phys. **27**, 330 (1957).

[10] R. J. Zollweg, Phys. Rev. **111**, 113 (1958).

samples are formed on a quartz plate which can be moved along a track to various stations. At the middle station are evaporators from which small amounts of the desired elements can be evaporated onto the sample holder. At the lower station is a tantalum cylinder which can be heated by induction, thus providing an oven for heat-treating the sample. The upper station is on the optic axis of a pair of quartz windows, where optical measurements can be made on the sample. In this third position, the sample is inside a copper block which may be cooled to liquid air temperature during the optical measurements.

The one-inch diameter quartz windows are sealed on with an epoxy resin.[11] This resin cement limits the outgassing temperature of these tubes to 125°C. Because of this some tubes were built with a section of the main body of the tube made of 9741 ultraviolet transmitting glass, which served as a window in place of the quartz. These tubes could be baked at the usual 450°C temperature and were used for preparation of the oxide and sulfide samples.

The samples were prepared by first evaporating a small amount of the desired alkaline earth metal onto the substrate and then introducing the VIB element on top of this. Three different procedures were required for selenium and tellurium, for sulfur, and for oxygen. Selenium and tellurium could be easily kept in evaporators and thus evaporated directly onto the alkaline earth metal film. After evaporation of the Se or Te, the sample holder was placed in the tantalum induction furnace and heated to cause chemical reaction and formation of the compound.

Sulfur had a higher vapor pressure and had to be kept in an ampule in a side arm until after evaporation of the alkaline earth metal film. The ampule could then be broken open and sulfur vapor admitted to the tube. The entire tube was then placed in an oven and baked to cause formation of the sulfide. Excess sulfur was then removed from the tube by condensing it in a side arm placed in liquid air.

Oxygen could be admitted to the tube through a silver side arm which becomes porous to oxygen when heated to about 800°C. Again, as for sulfur, the entire tube was heated to cause formation of the sample. Excess oxygen could then be removed by flashing a tantalum filment and a Batalum getter.

After the initial formation of the sample as described above, during which the sample was usually heated to about 300°C, it was necessary to anneal the sample. As the annealing temperatures for these materials were unknown, the samples were heated for one hour at successive 100°C intervals. The absorption spectrum after each heating was noted, and the best spectra obtained in this manner are presented here. Most of the samples annealed well at temperatures between 600 and 800°C. Heating to higher temperatures would cause destruction of the spectrum possibly due to the reaction

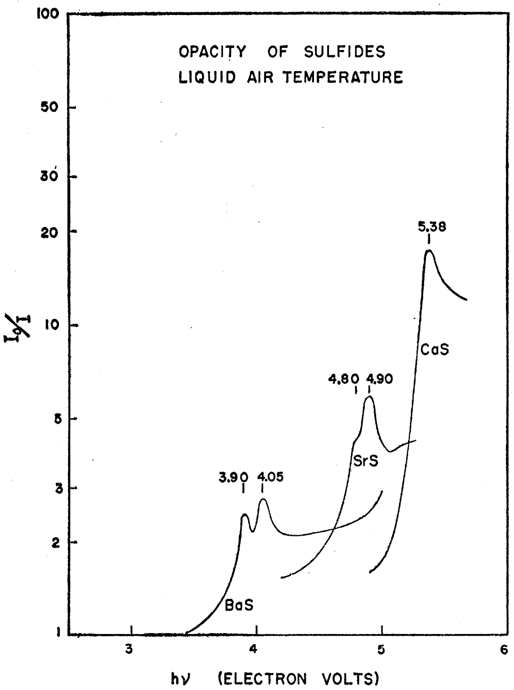

FIG. 2. Logarithm of opacity of alkaline earth sulfides measured at liquid air temperature.

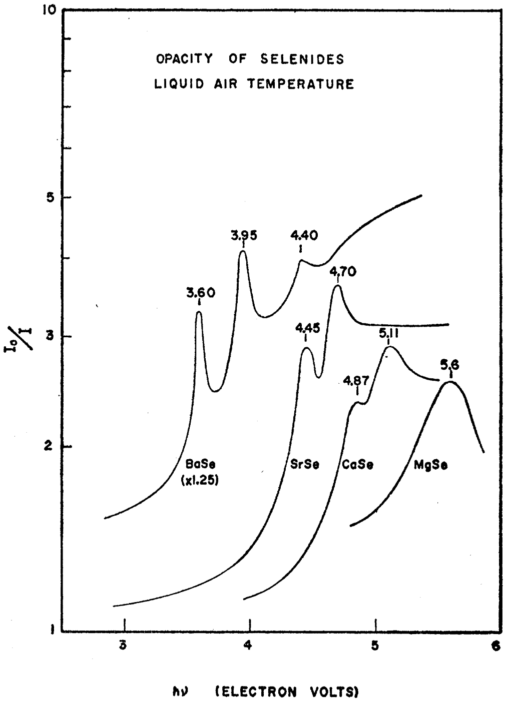

FIG. 3. Logarithm of opacity of alkaline earth selenides measured at liquid air temperature.

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[11] Hysol 2030 with type C hardener, obtained from Houghton Laboratories, Inc., Olean, New York.

TABLE I. Positions of optical absorption peaks.

Salt	Absorption peaks in ev			ΔE_{ob}[a]	ΔE_{ion}[b]
BaO[c]	4.10	4.38		0.28	0.025
SrO[c]	5.77			e	
MgO[d]	7.6		8.8	e	
BaS	3.90	4.05		0.15	0.065
SrS	4.80	4.90		0.10	
CaS	5.38			e	
BaSe	3.60	3.95	4.40	0.35	0.29
SrSe	4.45	4.70		0.25	
CaSe	4.87	5.11		0.24	
MgSe	5.6			f	
BaTe	3.10	3.65	4.08	0.55	0.65
SrTe	3.77	4.27		0.50	
CaTe	4.07	4.55		0.48	
MgTe	3.60	4.75		g	

[a] Observed separation of first peaks.
[b] Spin-orbit splitting of free ion obtained from Fig. 5.
[c] Measured at room temperature. All others measured at liquid air temperature.
[d] Data obtained by Reiling and Hensley (see reference 8).
[e] Not resolved.
[f] Second peak not observed probably due to instrumental limitation.
[g] Not applicable since MgTe has wurtzite structure.

of the sample with the substrate or residual gas in the tube.

EXPERIMENTAL RESULTS

As a check on the experimental methods employed here, samples of BaO and SrO were prepared and measurements made on them at room temperature. Little effort was made to anneal these samples. Absorption maxima were observed at 4.10 and 4.38 ev in BaO, and at 5.77 ev in SrO. These values are in good agreement with the room temperature values obtained by the earlier workers.[3–6]

Figures 2, 3, and 4 show plots of the opacities *vs* quantum energy for the sulfide, selenide, and telluride compounds. Some of the curves have been shifted vertically to prevent the lines from crossing each other. The spectra presented here are for annealed samples at liquid air temperature. The absorption peaks were found to sharpen both on annealing the sample and on cooling to liquid air temperatures.

Absolute values of the absorption constants are not given since the film thicknesses were not measured. However, an estimate of the absorption constants can be made as follows: The thin metal films transmitted about twenty percent of visible light before reacting. After reacting, the films transmitted about twenty percent of the light in the regions of maximum absorption. Thus the absorption constants in the fundamental region of these compounds are about the same magnitude as for metals, i.e., about 10^5 cm^{-1}.

DISCUSSION

The optical absorption bands observed are summarized in Table I. The interpretation of these bands has been discussed by Zollweg,[10] Overhauser,[12] Krumhansl,[13] and Goodman.[14] This structure is undoubtedly intrinsic to the pure compounds because of its independence to the purity of the materials and to the method of preparation. Evidence that this structure is due to the formation of excitons is based on the large value of the absorption constant, the fact that the peaks become sharper with decreasing temperature and the similarity to the structure observed in similar materials which has been correlated with excitons. The values obtained for the barium and strontium compounds are in good agreement[15] with those reported by Zollweg.[10]

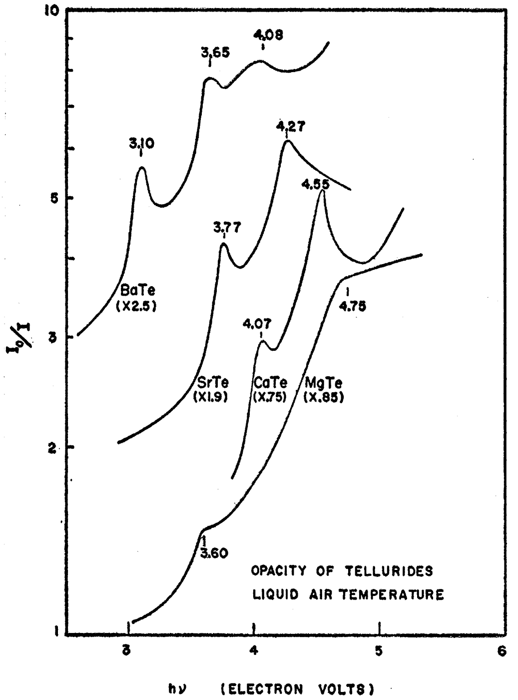

FIG. 4. Logarithm of opacity of alkaline earth tellurides measured at liquid air temperature.

From the data presented in Table I, it will be observed that the energy of the first absorption peak shifts to lower energies for increasing atomic number in either of the two columns of the periodic table. This is quite

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[12] A. W. Overhauser, Phys. Rev. **101**, 1702 (1956).

[13] J. A. Krumhansl, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 455.

[14] B. Goodman, *Proceedings of the 1958 International Conference on Semiconductors* (to be published).

[15] Zollweg's data are somewhat sharper and extends further into the ultraviolet than the data reported here. Although in his paper Zollweg suggests this may have resulted from his films being better annealed than ours, we believe this simply reflects the superior merits of a double monochromator such as used by Zollweg over the single-pass instrument we used. The larger fraction of scattered light present in a single-pass instrument makes it difficult to work with samples which have a transmission much less than 10%. The reduction of this scattered light in a double monochromator permits the use of thicker films which reduces the relative effect of reflection from the front surface of the film. This is clearly seen in Fig. 1 of Zollweg's paper in which the optical density is shown for a sequence of films of increasing thickness. Our data correspond most closely to the two lower curves in this figure.

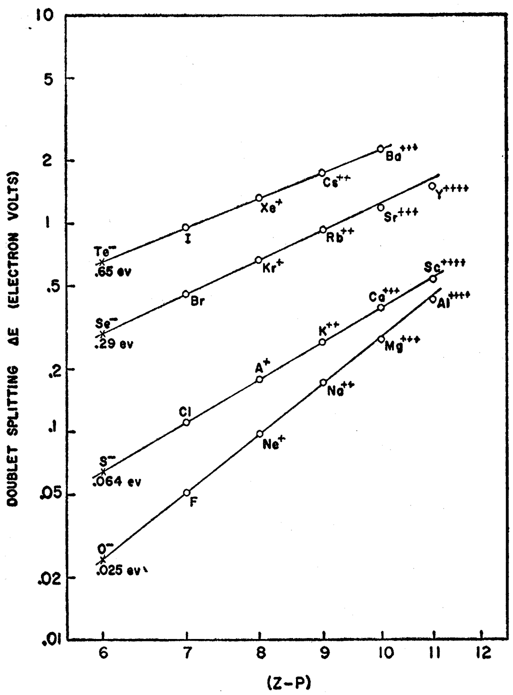

FIG. 5. Plots of the spin-orbit splittings ΔE of the ions in the isoelectronic series of O^-, S^-, Se^-, and Te^-. Z is the atomic number and p is the number of electrons in the completely filled shells.

different from the behavior in the alkali halides in which the energy of the first peak depends primarily on the halogen alone.

Many of the peaks in the observed spectra may be interpreted as doublets similar to those observed in the alkali halides.[16] This is consistent with the usual model for the formation of excitons in these materials in which an electron from one of the doubly charged negative ions is excited to a state localized on the neighboring positive ions. The ground state of the resulting singly charged negative ion may be split due to the spin-orbit interaction. To the extent that the wave function for the hole representing this missing electron is not influenced by the neighboring ions, this splitting will be similar to that occurring in a free ion.

Experimental values for the splitting in singly charged VIB negative ions are not available since their excited states are probably unstable. However, Vier and Mayer[17] estimated the splitting for the free O^- ions by plotting $\log\Delta E$ *vs* $\log(Z\text{-}p)$ for the O^- isoelectronic series, where ΔE is the doublet splitting, Z is the atomic number, and p is the number of electrons in the filled core shells. Following this procedure we made the plots shown in Fig. 5 for the isoelectronic series of O^-, S^-, Se^-, and Te^-. Values for the doublet splittings of the various ions appearing in this plot were obtained from the literature.[18] The extrapolated values for the splitting in the free VIB ions from these plots are shown in the last column of Table I.

The separation of the first two peaks of the observed spectra is interpreted as corresponding to the splitting discussed above and is listed in the next to the last column of Table I. For the selenides and tellurides there appears to be fairly good agreement with the values determined for the free ion listed in the last column. However for the heavier oxides and sulfides the observed splittings appear to be much larger than the free-ion values. Krumhansl[13] has suggested that this could be understood if the hole were partly associated with the neighboring metal ions since the heavier of these have a larger spin-orbit interaction. In support of this view, it is noted that the anomalous splitting decreases for decreasing atomic number of the metal ions.

ACKNOWLEDGMENT

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[16] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 99.

[17] D. Vier and J. Mayer, J. Chem. Phys. **12**, 28 (1949).

[18] R. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932); M. Fitzgerald and R. Sawyer, Phys. Rev. **46**, 576 (1934); P. Kruger and L. Phillips, Phys. Rev. **51**, 1087 (1937); D. Tomboulian, Phys. Rev. **54**, 350 (1938); F. Paul and W. Rense, Phys. Rev. **56**, 1110 (1939).