force constant model has also been studied by Clark[22] who has arrived at the same conclusion as is reached here. A more general force constant model has been applied to vanadium by Singh and Bowers,[7] but the elastic constants they used deviate considerably from the measured values.

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[22] C. B. Clark, Bull Am. Phys. Soc. 5, 41 (1960).

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The author is particularly indebted to D. K. Donald for preparing the single crystal specimens which made these measurements possible. Also, D. L. Waldorf deserves thanks for his help in orienting and cutting the acoustic specimens.

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Photoconductivity in Gallium Sulfo-Selenide Solid Solutions

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The photoconductivity characteristics of solid solutions of GaSe and GaS have been investigated for proportions of GaS between 10% and 50%. The difference between the room temperature band gaps of GaSe and GaSe(50)·GaS(50) is 73% of the total difference between the band gaps of GaSe (2.03 ev) and GaS (2.58 ev). The optical quenching energy and the thermal quenching energy of sensitizing centers are independent of the solid solution composition, thus giving additional evidence that these centers are associated with the crystal cation and that the photoconductivity observed is associated with holes.

INTRODUCTION

PHOTOCONDUCTIVITY in GaSe crystals has been described in a previous publication.[1] The major results of that investigation may be briefly summarized:

(1) GaSe has a layer-type crystal structure as indicated by easy cleavage perpendicular to the c axis.

(2) The photoconductivity characteristics of GaSe were not dependent on whether the applied field was parallel or perpendicular to the c axis.

(3) GaSe crystals were high conductivity p type as prepared from the melt, but low conductivity crystals with high photosensivity could be prepared by compensating with chlorine or tin impurity.

(4) Rectification tests at room temperature indicated photoconductivity by holes. Crystals were of too high a resistivity to permit Hall effect measurements to date.

(5) Both optical quenching and thermal quenching of photoconductivity were observed. The energy for optical quenching, about 1.0 ev, however, was twice the energy for thermal quenching, about 0.5 ev.

(6) Analysis of the thermal quenching data indicated a capture cross-section ratio for the sensitizing centers of 3×10^6.

GaS has the same crystal structure as GaSe[2] and a complete range of solid solutions should be possible. Evidence has been obtained from analysis of the properties of Group II-Group VI compounds indicating that the ionization energy of donor imperfections is associated primarily with the cation of the compound, and that the ionization energy of acceptor imperfections is associated primarily with the anion of the compound.[3] It is reasonable that a similar correlation should exist in the properties of Group III-Group VI compounds. It would be expected therefore, to find a variation in the ionization energy of the sensitizing centers with composition in GaSe·GaS solid solutions if the sensitizing centers were associated with acceptor-type imperfections (as is found in the CdSe·CdS system), but not if the sensitizing centers were associated with donor-type imperfections. Normally one would expect sensitizing centers to be associated with acceptor-type imperfections (negatively charged) if the photocurrent were carried primarily by electrons (as in CdS and CdSe), and with donor-type imperfections (positively charged) if the photocurrent were carried primarily by holes. If the photocurrent in GaSe is carried by holes, therefore, as indicated by the previous investigation, it would be expected that the ionization energy of sensitizing centers would be relatively independent of composition in GaSe·GaS solid solutions. It is the purpose of this paper to present the results which confirm this expectation.

EXPERIMENTAL

Crystals of GaSe·GaS solid solutions were grown in essentially the same manner as described previously for the growth of GaSe crystals.[1] Reaction between the elements was followed by gradient freeze crystallization. Since the melting points of GaSe (960°C) and GaS (about 1020°C) are not appreciably different, all solid solutions had melting points within a small temperature

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[1] R. H. Bube and E. L. Lind, Phys. Rev. 115, 1159 (1959).

[2] H. Hahn and G. Frank, Z. anorg. u. allgem. Chem. 278, 340 (1955).

[3] R. H. Bube and E. L. Lind, Phys. Rev. 110, 1040 (1958).

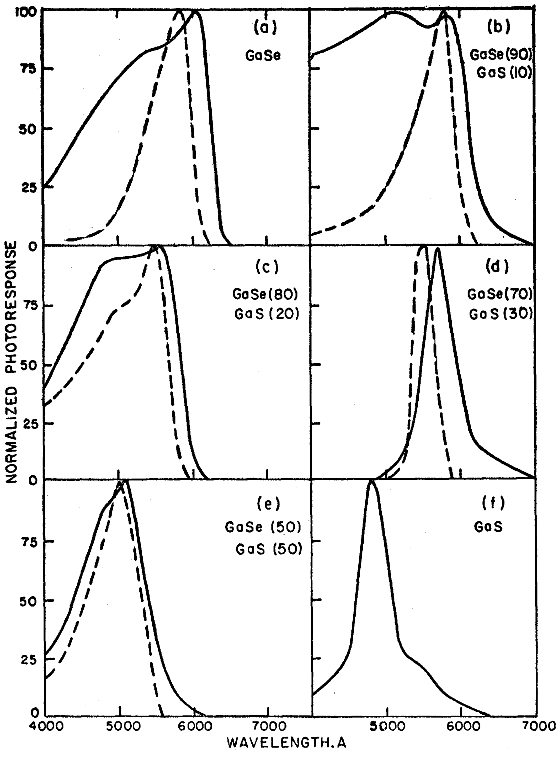

FIG. 1. Spectral response of photoconductivity at 300°K (solid curves) and 90°K (dashed curves), for various ratios in the GaSe·GaS solid solution sequence.

range. Slower cooling was used to get good solid-solution single crystals than was necessary for the GaSe; about 40 hours was used to decrease the temperature to 120°C below the melting point. Impurity compensation was accomplished by addition of metallic Sn to the initial melt.

Difficulties of preparation without explosion above 50% GaS postponed further measurements in this range until suitable pressure apparatus is available. Single crystals of GaS, however, were obtained by similar preparation procedures and were available for comparison.[4] The data at hand indicate that most of the results of interest occur for proportions of GaS less than 50%.

TABLE I. Summary of data.

GaSe(x)·GaS($1-x$) x	Band gap, ev 300°K	90°K	$\frac{\partial E_G}{\partial T}$, ev/deg $\times 10^{-4}$	E_{opt}^*, ev	E_{th}^*, ev	τ_{maj}, μ sec[a]
1.0	2.03	2.12	−4.3	1.05	0.54	6000
0.9	2.09	2.16	−3.3	1.14	0.57	450
0.8	2.19	2.25	−2.9	1.14	0.57	450
0.7	2.19	2.26	−3.3	1.13	0.59	200
0.5	2.43	2.48	−2.4	1.14	(0.68)	20
0	2.58	···	···	···	···	0.1

[a] Approximate maximum majority carrier lifetime observed, assuming mobility of 10 cm^2/volt sec.

Photoconductivity measurements were made with melted indium contacts, tested to insure ohmic behavior, in an atmosphere of He gas between the temperatures of 90° and 400°K. Excitation was primarily by a Bausch and Lomb grating monochromator.

RESULTS

A summary of the data is given in Table I, where are listed the band gaps at 300° and 90°K, the corresponding temperature coefficients of band gap, the optical quenching energy for photoconductivity, and the thermal quenching energy for photoconductivity.

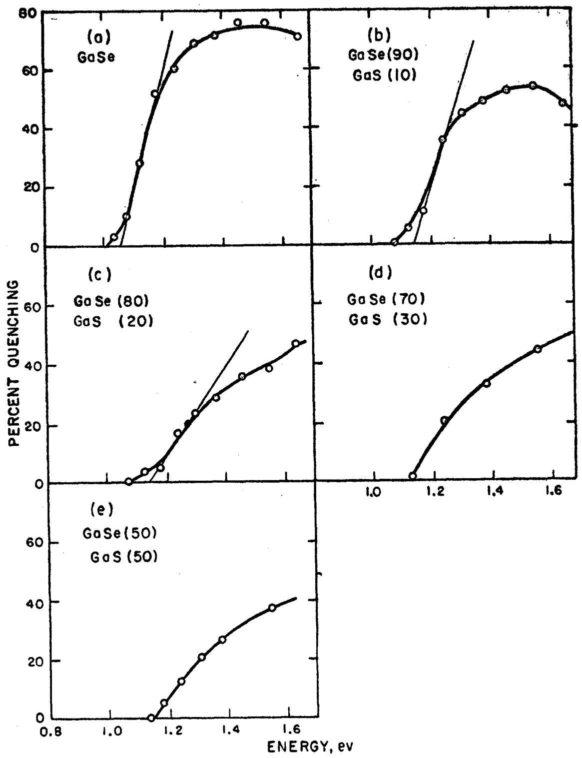

FIG. 2. Optical quenching spectra at 90°K for various ratios in the GaSe·GaS solid solution sequence.

Band Gaps

Figure 1 shows the photoconductivity excitation spectra of the various solid-solution compounds, compared with those of GaSe and GaS. The maxima of the curves have been selected as a measure of the band gap; the values obtained in this way are probably reliable to a few hundredths of a volt.

Optical Quenching

Optical quenching of photoconductivity was measured at 90°K with the results shown in Fig. 2. Although the shape of the quenching spectrum is altered with increasing proportion of GaS, the low-energy threshold is approximately unchanged. The photosen-

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[4] Grown by I. J. Hegyi; supplied by E. E. Loebner.

sitivity of the GaS crystal at low temperatures was too low to permit measurement of optical quenching.

Thermal Quenching

The variation of photocurrent with temperature for comparable excitation conditions is shown in Fig. 3 for GaSe and the GaSe·GaS solid solutions. Included also is the same type of variation for the GaS crystal, measured with a somewhat more intense light source. A rate equation analysis described elsewhere[5] was used in the previous investigation[1] to obtain values of the thermal quenching energy and sensitizing center cross-section ratio for the GaSe crystas. This same cross-section ratio was assumed to hold for the other members of the GaSe·GaS solid solutions, and the sensitizing center thermal ionization energy was calculated for each from the temperature and conductivity at the temperature breakpoint. It is directly discernible from inspection of Fig. 3 that the temperature breakpoint is relatively independent of the solid-solution composition. The corresponding calculated values of thermal ionization energy also show little dependence on solid-solution composition.

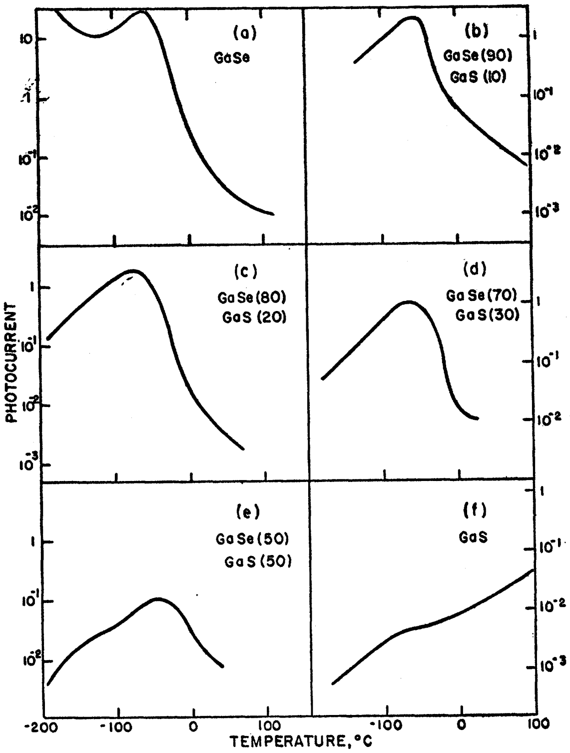

FIG. 3. Temperature dependence of photocurrent for various ratios in the GaSe·GaS solid solution sequence. For Sec. (a) through (e), excitation is by a broad band from a monochromator centered about the excitation maximum; for Sec. (f) excitation is by a 900 ft-c incandescent light source. All measurements made for an applied voltage of 10 volts.

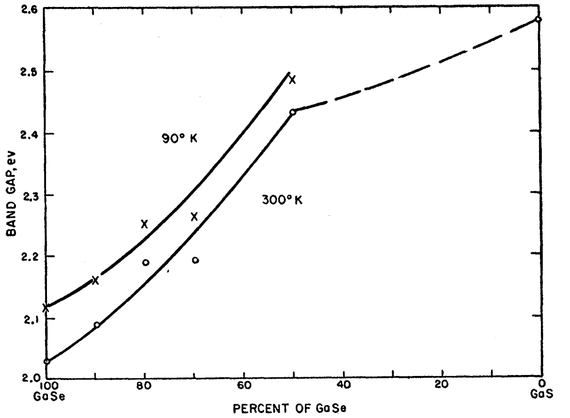

FIG. 4. Dependence of the band gap as determined from photoconductivity excitation spectra at 300°K and 90°K on the composition of GaSe·GaS solid solutions.

The effect of increasing proportion of GaS is to (1) decrease the photosensitivity, and (2) decrease correspondingly the ratio of maximum photocurrent at the temperature breakpoint and the high-temperature reduced photocurrent. It may be noted from Fig. 3 that the materials indicated in Fig 3(a) through 3(e) all have about the same high-temperature photosensitivity, not very much different from the high-temperature photosensitivity of GaS itself. The addition of GaS may be interpreted either as decreasing the cross-section ratio of the sensitizing centers, or as decreasing the density of sensitizing centers relative to efficient recombination centers. It is likely, therefore, that the apparent small increase in thermal ionization energy for the GaSe(50)·GaS(50) compound is not a real increase; a reduction in the cross-section ratio of the sensitizing centers would account for the observed effect.

DISCUSSION

The dependence of band gap on the composition of the GaSe·GaS solid solution is shown in Fig. 4. A concave upwards variation is indicated between GaSe and GaSe(50)·GaS(50), with the band gap of the latter compound being 73% of the difference between the band gaps of GaSe and GaS. Thus the variation of band gap with composition bears at least a superficial similarity to the type of variation find in the Ge·Si system.[6]

The invariability of the optical quenching energy and the thermal quenching energy with the composition of the solid solution is additional evidence that the sensitizing centers are associated with donor-type imperfections and that the photocurrents are carried primarily by holes.

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[5] R. H. Bube, J. Phys. Chem. Solids **1**, 234 (1957).

[6] R. Braunstein, A. R. Moore, and F. Herman, Phys. Rev. **109**, 695 (1958).