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Optical absorption, electrical conductivity and spectral response measurements on the system $CdGa_2S_{4(1-x)}Se_{4x}$

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The compounds $CdGa_2S_4$ and $CdGa_2Se_4$ belong to the defect chalcopyrite (space group $I\bar{4}$) family. A series of compounds $CdGa_2S_{4(1-x)}Se_{4x}$ has been prepared and their single crystals grown by the chemical transport reaction method. Optical absorption, spectral response, electrical conductivity and thermoelectric power measurements have been made. The optical absorption spectra revealed that the fundamental absorption edge varies with composition, from 2.2 to 3.25 eV. The plots $(\alpha\hbar w)^2$ versus $\hbar w$ revealed that these compounds are direct band gap materials, but plots of $(\alpha\hbar w)^{1/2}$ versus $\hbar w$ did not give convincing support to the presence of indirect transitions. The values of energy gaps were also deduced from spectral response (λmax) measurements and found to be in agreement with those deduced from optical absorption measurements. D.c. resistivity versus temperature studies revealed that, in spite of their large band gaps, these compounds exhibit intrinsic semiconduction above 250° C. The energy gap values matched with those obtained from other measurements. All samples were n-type and had a constant thermoelectric power $\approx 300\,\mu V\,°C^{-1}$ in the temperature range 250 to 350° C. However, the thermal dependence of electrical conductivity and thermoelectric power indicated strong irreversibility with the thermal heating and cooling cycle. Such behaviour has been attributed to the diffusion of contact materials such Ga and In.

1. Introduction

Semiconducting ternary compounds and their mixed crystals are particularly interesting due to the possibility of having series of materials where the band gap (E_g) varies with composition. Many ternary compounds display properties such as photoconductivity and electroluminescence similar to those of the traditional binary semiconductors. The compounds $CdGa_2S_4$ and $CdGa_2Se_4$ are analogues of the binary II–VI compounds, and their optical absorptions and spectral response of photoconductivity have been studied by some workers. These compounds are known to crystalize in tetragonal structure of thiogallate [1] (defect chalcopyrite) with the space group ($I\bar{4} - S_4^2$), and single crystals of these compounds can be grown by the chemical transport reaction (CTR) [2] method. Optical absorption studies by Beun *et al.* [3] and Abdullaev *et al.* [4] showed that $CdGa_2S_4$ and $CdGa_2Se_4$ have direct band gaps of 3.44 and 2.41 eV, respectively, and indirect band gaps of 3.40 and 2.27 eV, respectively. However, Streltosov *et al.* [5] reported E_g(dir) for $CdGa_2Se_4$ to have a value of 2.1 eV, and that this value varied with non-stoichiometric composition of the crystals obtained by the CTR method.

Reflection spectra [6] of these compounds indicated high values of E_g(dir) (e.g. $CdGa_2S_4$ $E_g(\text{dir}) = 3.58$ eV, $CdGa_2Se_4$ $E_g(\text{dir}) = 2.55$ eV) and exhibited some additional peaks beyond Eg(dir) which were attributed to the valence–sub-band transitions. These optical band gaps were also confirmed from the spectral response of photoconductivity [3, 7].

However, there are no systematic basic studies of transport properties of these compounds. We have made detailed studies of structural, optical absorption, spectral response of photoconductivity, thermal dependence of conductivity and thermoelectric properties of these two compounds and their solid solutions represented by the chemical formula $CdGa_2S_{4(1-x)}Se_{4x}$, where $x = 0.00$, 0.25, 0.5, 0.75 and 1.0. The preparation, crystal growth and crystallographic studies of this system are published elsewhere [8].

In this paper we report our results on measurements of optical absorption and transport properties of this system.

2. Experimental

The single crystals used in this study were grown by the CTR method [8]. Single crystal specimens for optical absorption were prepared by waxing the crystal with its naturally grown face [(0 0 1) for $CdGa_2S_4$ and $CdGa_2S_3Se$ and (1 1 2) for other compositions] with an optically flat glass plate and grinding off the rest using SiC-abrasives of various grades (300, 400, 600). Finally, the ground face was polished by rubbing slowly on a teflon sheet lubricated with a drop of 5% solution of conc. HNO_3 : HF(40%), 50 : 50, in water and then washed ultrasonically. Owing to the brittle nature of the crystals, the minimum thickness to which crystals could be ground was limited to $100\,\mu m$. The thickness was measured by the weight method. Optical absorption measurements were made on Unicam SP500 and Perkin-Elmer 350 spectrophotometers.

Single crystal specimens for measurement of electrical properties were prepared by lapping the crystals to provide two parallel surfaces. Indium–Gallium eutectic contacts were applied to both ground surfaces by rubbing the indium stick and a very small drop of Ga together. The crystals were then annealed in vacuum at 300° C for 10 to 20 min. For electrical conductivity measurements the crystal was fixed between two graphite spacers to which electrodes were attached. The sample-holding electrodes were fixed to a sapphire plate.

The resistance was measured using a stabilized d.c. power supply (0 to 300 V) and a high sensitivity d.c. microvoltmeter (Philips PP 9004). The spectral response measurements were made by using a tungsten lamp of known emissivity characteristics and interference optical filters (in steps, 350, 375 to 1000 nm) of known spectral and transmission characteristics.

The thermoelectric measurements were made by using a electrometer operational amplifier (3431 J–K, Burr-Brown, USA) in the temperature

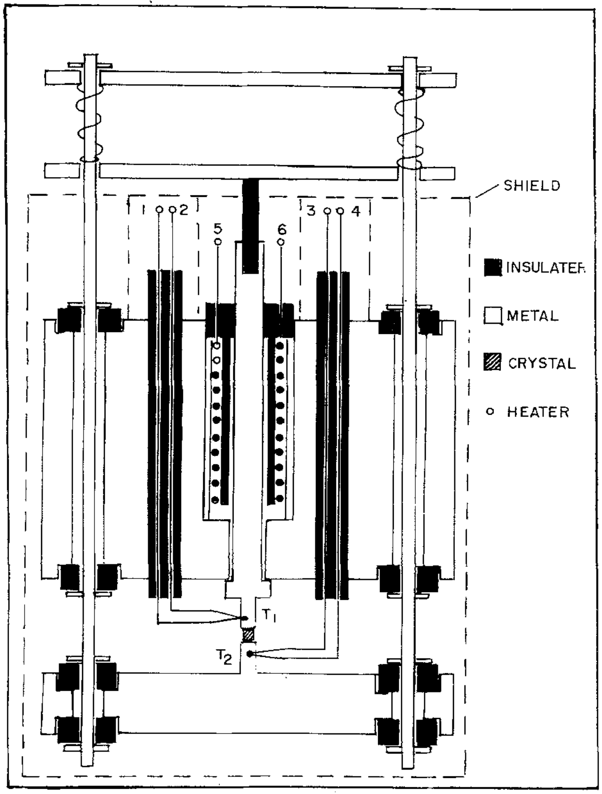

Figure 1 Schematic diagram of the sample holder for the thermoelectric power measurements.

range 250 to 350° C. This allowed the measurements only up to impedence levels of $10^9\,\Omega$. Above $10^9\,\Omega$ the pick-up levels could not be eliminated.

Because of the high impedence levels at which these amplifiers operate, extreme care was taken by using proper shielding arrangements to reduce the noise pick-up. A good insulation of the components and wiring associated with the input signal terminals was ensured by using teflon stand-off.

The sample holder used for the measurements of thermoelectric power is shown in Fig. 1. Two chromel–alumel thermocouples were fused to the electrodes and used to measure the temperatures at both ends of the sample. The t.e.m.f. generated due to temperature difference was measured across terminals 1 and 2. Since In–Ga contacts were deposited on the two parallel faces of the crystals, thin graphite spacers were used to protect against deterioration of the contacts. The temperature of the sample was varied using a conventional differential temperature furnace, providing a temperature difference per cm of 10 to 20° C. The zero t.e.m.f. across the sample was obtained by compensating this temperature difference by energizing the micro-heater situated at one end. The t.e.m.f. measurements were limited by the unavoidable lengths of the electrode wires forming large interelectrode capacitance when sample resistance was greater than $10^9\,\Omega$.

3. Results and discussion

As indicated in Section 1 a considerable variation has been observed in reported values of band gaps of $CdGa_2S_4$ and $CdGa_2Se_4$. Such a variation has been attributed to the non-stoichiometric compositions of the crystals. It is also known from literature that the band gap varies with the direction in the crystals along which the absorption or reflection spectra were studied. However, previous workers have not identified the faces for which they studied the optical absorption or reflection spectra: this may be an additional reason for the observed scatter in the values of energy band gaps of these two compounds. In our present investigation, we have identified the faces for which we have studied the optical absorption as a function of wavelength by Lane back-reflection photography

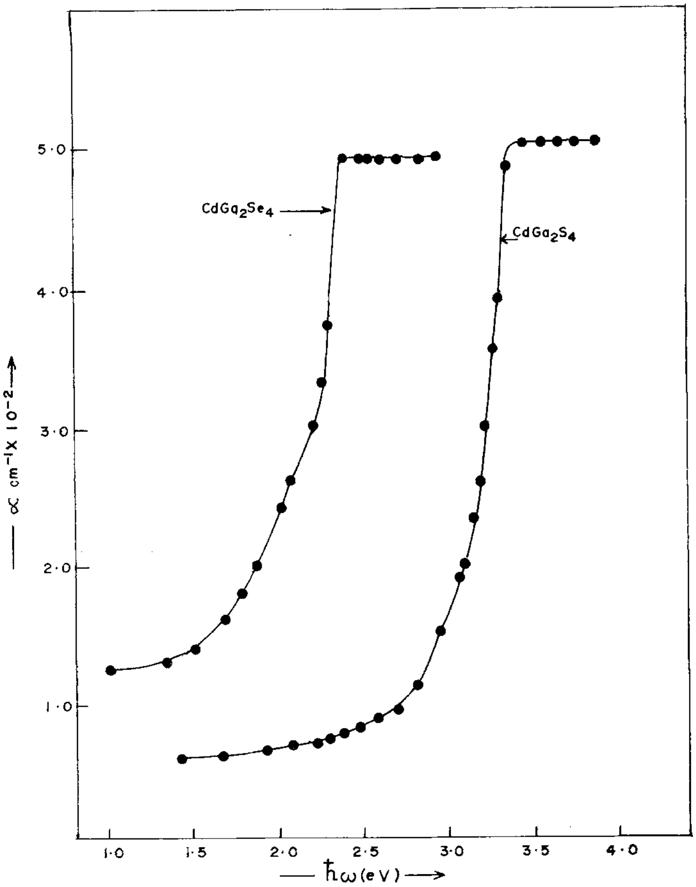

Figure 2 Variations of optical absorption coefficient as a function of photon energy for $CdGa_2S_4$ and $CdGa_2Se_4$.

[8]. $CdGa_2S_4$ and $CdGa_2S_3Se$ were polyhedral crystals with the biggest face parallel to (0 0 1), whereas $CdGa_2S_2Se_2$, $CdGa_2SSe_3$ and $CdGa_2Se_4$ were triangular prisms with edge ⟨1 1 0⟩ and a face parallel to the (1 1 2) plane.

For $CdGa_2S_4$, Buen *et al.* [3] reported wave lengths at which α (the optical absorption coefficient) = 500 cm^{-1} as fundamental absorption edge, λ_{edge} = 358 nm (i.e. 3.45 eV), and did not give any further analysis of the absorption spectrum.

The spectral dependence of the absorption coefficient, calculated from our measurements on transmission through single crystals of $CdGa_2S_4$ with the (0 0 1) face normal to the incident light beam, is shown in Fig. 2. The edge of the absorption band of $CdGa_2S_4$ occurs at 400 nm, which corresponds to an energy of 3.1 eV and $\alpha = 200$ cm^{-1}. Further analysis of this spectrum was made assuming that the absorption spectrum beyond the absorption edge is caused by the direct transitions of electrons between a valence band maximum (at $K = 0$) and a conduction band minimum (at $K = 0$). The spectrum may then be considered theoretically to obey the equation [2, 3, 9]:

$$\alpha_d = \frac{\text{constant} \times [\hbar w - E_g(\text{dir})]^{1/2}}{\hbar w} \qquad (1)$$

which is true only for $\hbar w > E_g(\text{dir})$ and $\alpha_d = 0$ when $\hbar w < E_g(\text{dir})$. The minimum energy gap for direct transitions to occur may then be obtained by extrapolating the straight line plots of $(\alpha \hbar w)^2$ versus $\hbar w$ to $\alpha_d = 0$. In the case of $CdGa_2S_4$ (Fig. 3) the energy gap $E_g(\text{dir})$ obtained is 3.25 eV.

Further more, assuming that the absorption spectrum before and near the absorption edge is caused by the indirect transitions of electrons between a valence band maximum at ($K = 0$) and a conduction band minimum at ($K \neq 0$), the spectrum was thought to obey the following equation [9]:

$$\alpha_i = \alpha_i(\text{I}) + \alpha_i(\text{II})$$

where $\alpha_i(\text{I})$ is the absorption coefficient due to phonon emission and $\alpha_i(\text{II})$ is due to the phonon absorption and

$$\alpha_i(\text{I}) = \frac{\text{constant} \times [\hbar w + E_p - E_g(\text{indir})]^2}{\hbar w} \qquad (2)$$

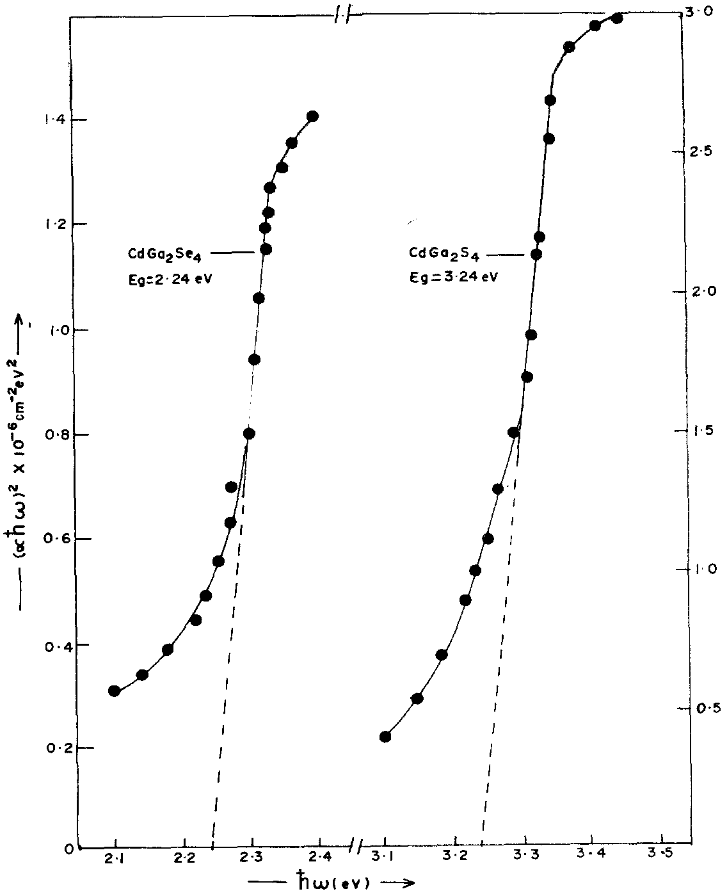

Figure 3 Variation of $(\alpha\hbar w)^2$ as a function of photon energy for $CdGa_2S_4$ and $CdGa_2Se_4$.

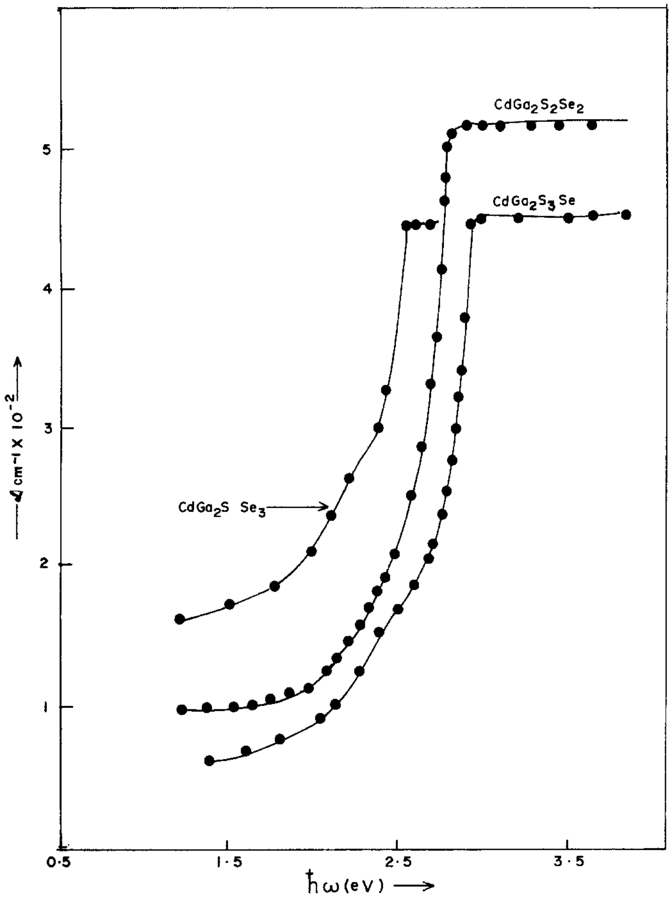

Figure 4 Variation of optical absorption coefficient as a function of photon energy for $CdGa_2S_3Se$, $CdGa_2S_2Se_2$ and $CdGa_2SSe_3$.

which is true for $\hbar w > E_g(\text{indir}) - E_p$, and $\alpha_i(\text{I}) = 0$, for $\hbar w < E_g - E_p$.

$$\alpha_i(\text{II}) = \frac{\text{constant} \times [\hbar w - E_p - E_g(\text{indir})]^2}{\hbar w} \qquad (3)$$

is true for $\hbar w > E_g + E_p$ and $\alpha_i(\text{II}) = 0$ when $\hbar w < E_g + E_p$.

Since the strong absorption due to the direct transition overlaps the weak absorption due to the indirect transitions near the funadmental absorption edge, the deduction of indirect band gaps needs careful and accurate analysis of the spectrum. We have plotted $(\alpha_i \hbar w)^{1/2}$ versus $\hbar w$ for values of α_i less than (the direct transition) 3.25 eV for $CdGa_2S_4$. However, the plot did not yield convincing evidence for the presence of indirect transitions, which is not in agreement with Beun *et al.* Our data are supported by the reflectivity study of $CdGa_2S_4$ [6] where no peaks corresponding to the indirect transtion were observed.

On the other hand, Radautsan *et al* [7] analysed the absorption spectrum of $CdGa_2Se_4$. They supported data of Beun *et al.* [3] and obtained $E_g(\text{dir}) = 2.43$ eV and $E_g(\text{indir}) = 2.27$ eV. However, the analysis of indirect transition given by Radautsan *et al.* is rather misleading, as the energy ranges of the absorption spectrum for the indirect and direct transitions were not considered separately, and hence the $\alpha^{1/2}$ is most likely to contain values due direct transitions. Buen *et al* [3] have indicated the inadequacy of their data to support indirect transitions in this compound also. We have therefore carefully analysed our data of the absorption spectrum of $CdGa_2Se_4$ (Fig. 2). The plots of $(\alpha\hbar w)^2$ versus $\hbar w$ (Fig. 3) gave $E_g(\text{dir}) = 2.25$ eV whereas plots of $(\alpha\hbar w)^{1/2}$ versus $\hbar w$ for $\hbar w < 2.25$ eV did not give convincing support for indirect transitions. This is also in agreement with the reflectivity data of [4] where no peak due to indirect transitions was present.

However, we have, observed values of direct band gaps lower than those of Buen *et al.* and Radautson *et al.* The reasons for such an observation are unknown.

The spectral dependence of the absorption coefficients of the single crystal specimens of $CdGa_2S_3Se$ [for the (0 0 1) face], $CdGa_2S_2Se_2$

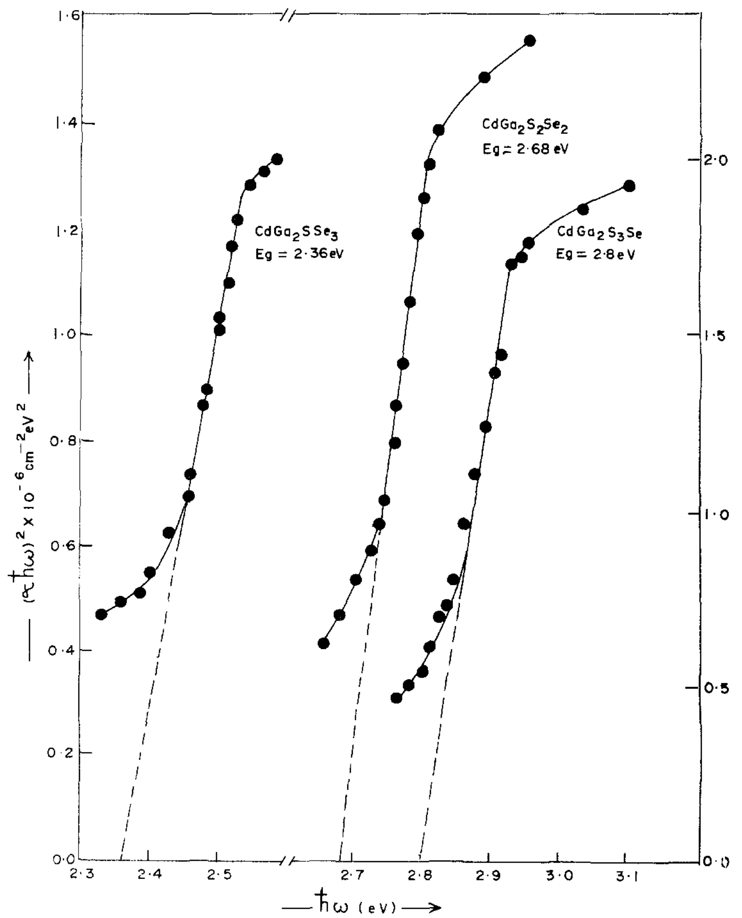

Figure 5 Variation of $(\alpha\hbar w)^2$ as a function of photon energy for $CdGa_2S_3Se$, $CdGa_2S_2Se_2$, $CdGa_2SSe_3$.

[for the (1 1 2) face] and $CdGa_2SSe_3$ [for the (1 1 2) face)] are presented in Fig. 4. There is slow rise in absorption in the long-wave region followed by a steep rise in the short-wave region. The spectra are isomorphous with those of the parent compounds (Figs. 2 and 4). The absorption edge was taken at the start of the steep rise and has values of 2.8, 2.65 and 2.45 eV for these compounds, respectively.

The variation of $(\alpha\hbar w)^2$ as a function of $\hbar w$ for These new compositions has been plotted in Fig. 5 The values of direct energy gaps obtained from these plots are 2.80, 2.67 and 2.37 eV for $CdGa_2S_3Se$, $CdGa_2S_2Se_2$ and $CdGa_2SSe_3$, respectively. The plots of $(\alpha\hbar w)^{1/2}$ versus $\hbar w$ did not convincingly support the presence of indirect transition.

All compositions exhibited very high dark resistivity (at 25° C) of the order of 10^{12} to $10^{13}\,\Omega$ cm. Photoconductivity was observed only when the In–Ga contacts were annealed at 300° C. The photoconductivity response was found to vary linearly with light intensity, which was tested by varying the power supply to the tungsten lamp.

The spectral response of photoconductivity of $CdGa_2S_4$ (Fig. 6) exhibited a narrow peak at 3.35 eV, which corresponds to the optical band gap (i.e. 3.25 eV). On the other hand, the photoconductivity spectrum of $CdGa_2Se_4$ (Fig. 6) exhibited peaks at 3.3, 2.92 and 2.58 eV. The last peak may be attributed to the optical band gap (i.e. 2.25 eV) whereas the peaks at 2.92 and 3.3 eV are thought to arise from electronic transitions between the valence sub-bands and the conduction band. Although the nature of the plots is in agreement with those of the Abdullaev *et al.* [10, 11] the energy values observed here are higher than theirs.

Photoconductivity spectra of the new compositions $CdGa_2S_3Se$, $CdGa_2S_2Se_2$ and $CdGa_2SSe_3$ are shown in Fig. 7. For each spectrum there are two peaks at the higher energy side in addition to that corresponding to the intrinsic minimum band gap. The positions of these peaks are given in Table I. The appearance of higher energy peaks beyond the optical band gap indicates a sub-band structure of the valence band of these compounds.

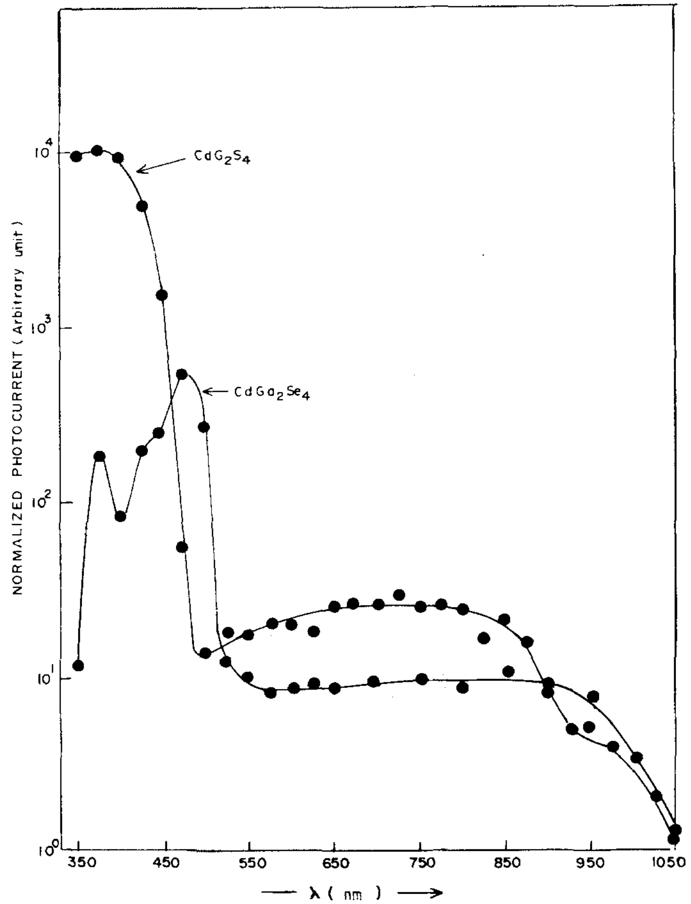

Figure 6 Spectral response of photoconductivity as a function of wavelength for $CdGa_2S_4$ and $CdGa_2Se_4$.

TABLE I

Compound	Peak corresponding to E_g(optical)	Peak II	Peak III
$CdGa_2S_4$	3.35	–	–
$CdGa_2S_3Se$	3.03	–	2.53
$CdGa_2S_2Se_2$	2.85	3.27	2.48
$CdGaSSe_3$	2.70	3.18	2.07
$CdGa_2Se_4$	2.58	3.30	2.82

All samples exhibited a diffuse peak in photoconductivity spectrum from the long-wave side increasing from 1050 nm to 850 nm and remaining constant overall up to 650 nm and then decreasing to 550 nm. Such behaviour is characteristic of a number of localized energy levels in the forbidden gap, and such energy states generally arise from a variety of defects. In the present case, they could arise from a small departure from stoichiometry or from position disorder arising from exchange of atoms between Cd and Ga sites.

The long-wave tail in the absorption spectrum may be attributed to this diffuse broad peak in photoconductivity spectra. The extrinsic defects which give rise to the diffuse absorption and the tail in the photoconductivity are probably responsible for the temperature independent part of the conductivity graph at low temperatures (< 200° C).

Plots of log R versus 1/T for all these compositions are shown in Figs. 8–12. The electrical conductivity exhibited no change in the temperature range 25 to 250° C. It increased with temperature up to 300° C and more quickly above 300 to 350° C. After cooling the sample to room temperature, a set of readings was again recorded for the second run on heating from 25 to 350° C. The activation energy as calculated from the slope of log R versus $1/T$ matched the half of the optical band gap for the first run, but was found to increase in the second run. Further increase in activation was also found when the readings were recorded a third time when heating from 25 to 350° C. The various values of activation energy are recorded in Table II.

The most interesting feature of the electrical conductivity data is that the compounds, in spite of their large band gaps, exhibit intrinsic conduc-

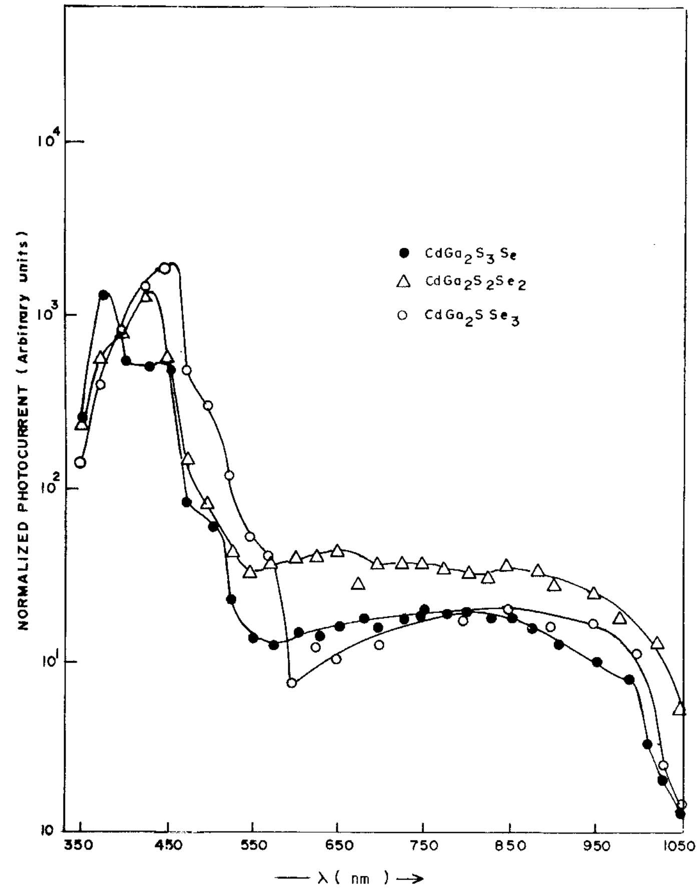

Figure 7 Spectral response of photoconductivity as a function of wavelength for $CdGa_2S_3Se$, $CdGa_2S_2Se_2$ and $CdGa_2SSe_3$.

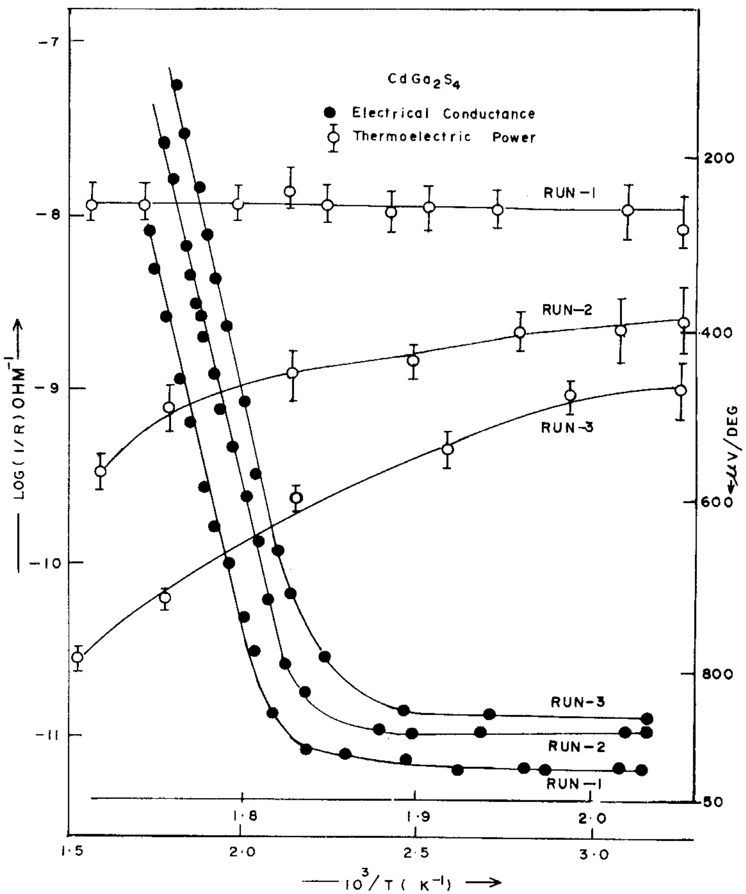

Figure 8 Temperature dependence of electrical conductivity and thermoelectric power of $CdGa_2S_4$.

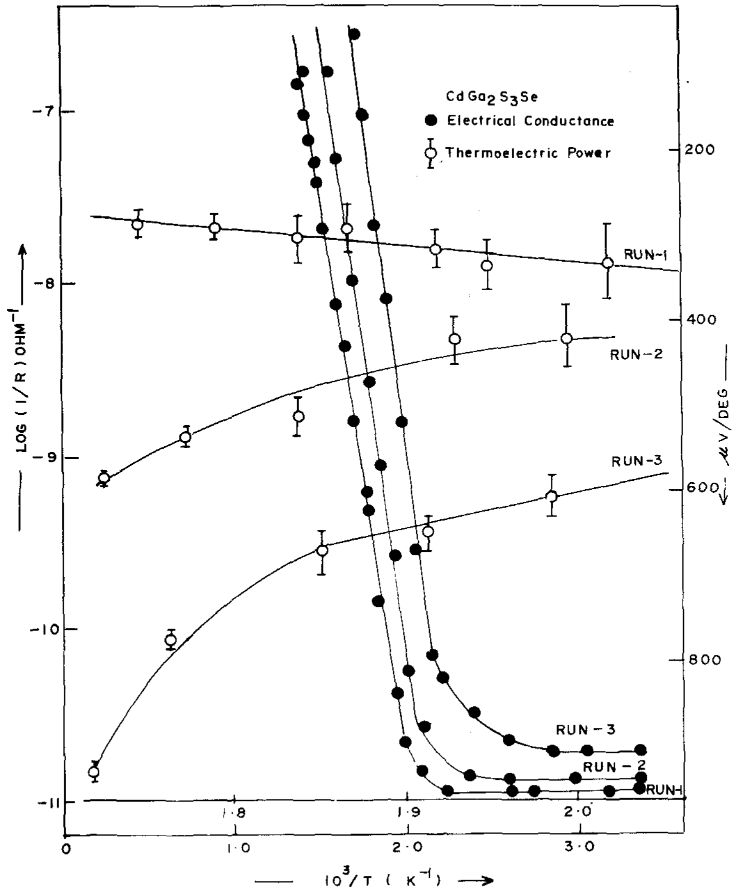

Figure 9 Temperature dependence of electrical conductivity and thermoelectric power of CdGa$_2$S$_3$Se.

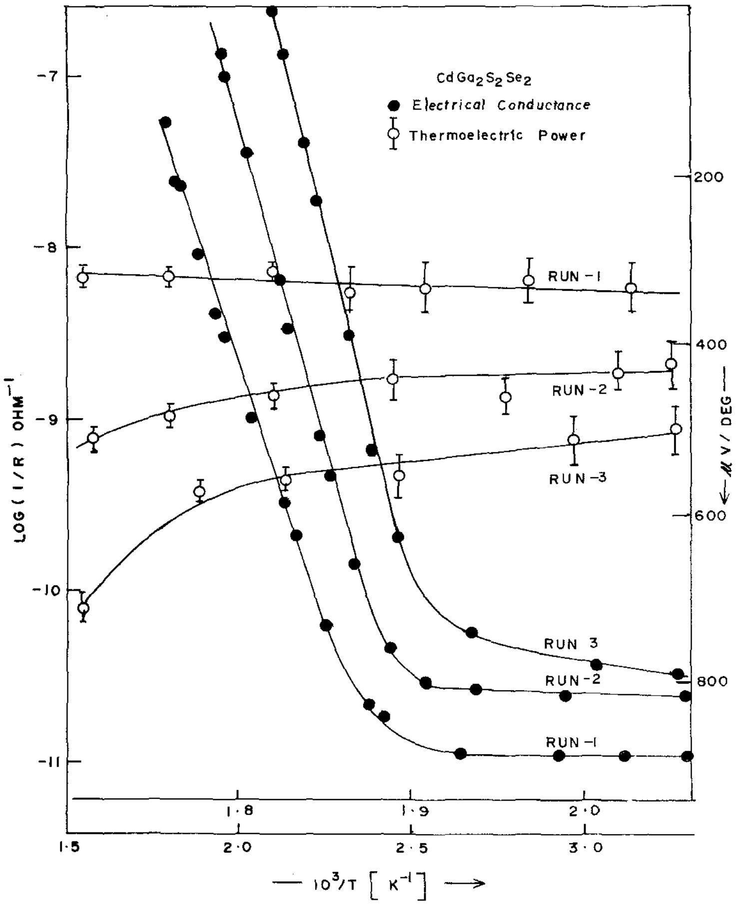

Figure 10 Temperature dependence of electrical conductivity and thermoelectric power of CdGa$_2$S$_2$Se$_1$.

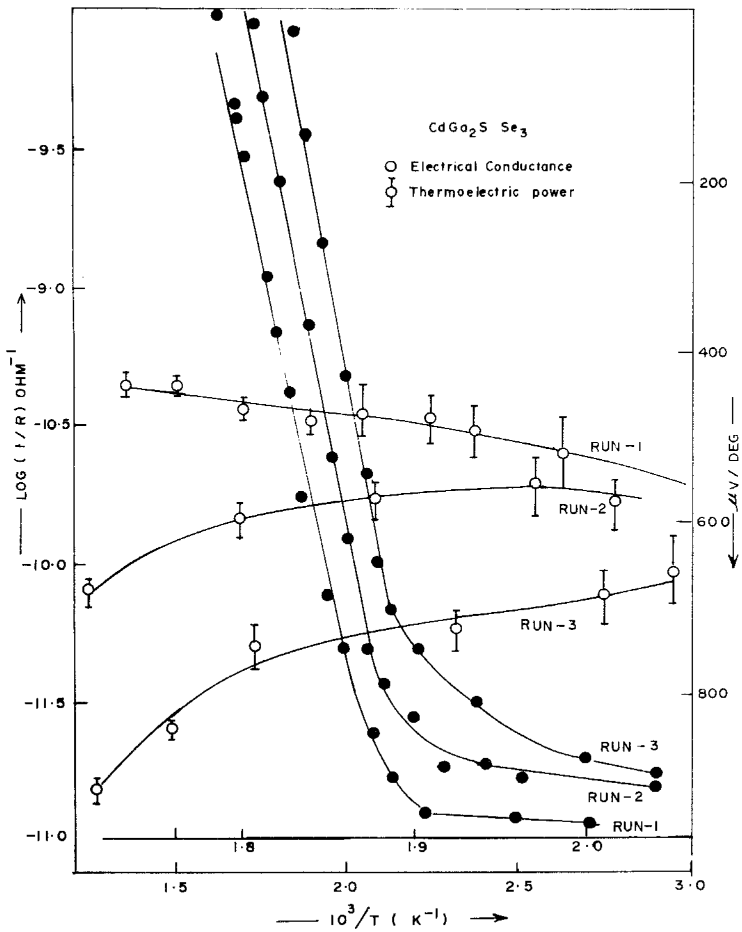

Figure 11 Temperature dependence of electrical conductivity and thermoelectric power of $CdGa_2SSe_3$.

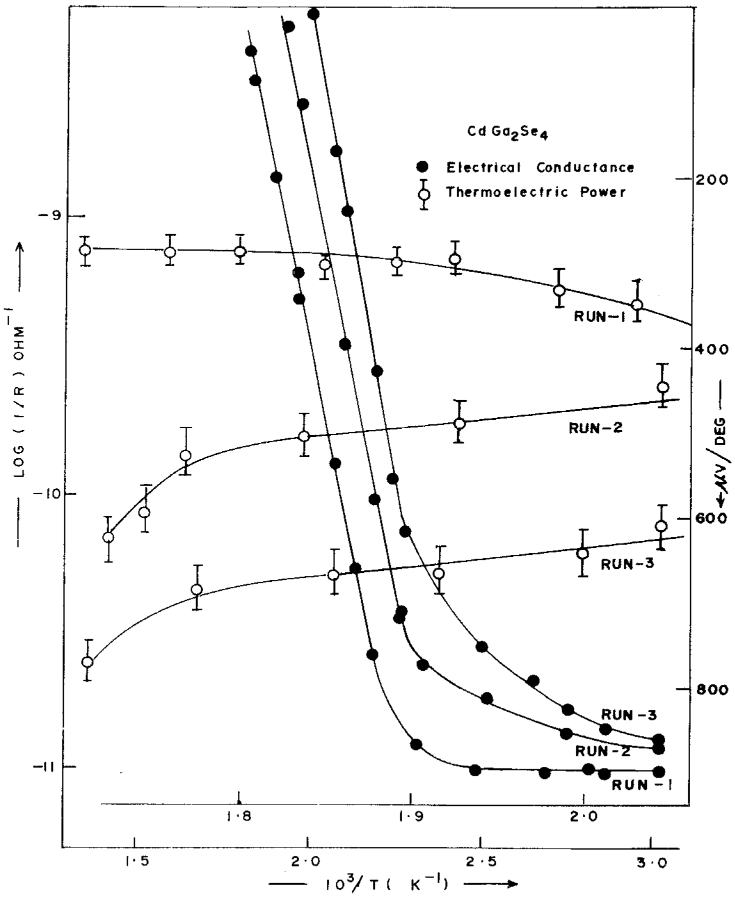

Figure 12 Temperature dependence of electrical conductivity and thermoelectric power for $CdGa_2Se_4$.

TABLE II Activation energy values (eV)

Compound	Run I	Run II	Run III
$CdGa_2S_4$	1.508	1.648	1.738
$CdGa_2S_3Se$	1.390	1.528	1.662
$CdGa_2S_2Se_2$	1.270	1.385	1.655
$CdGa_2SSe_3$	1.200	1.290	1.360
$CdGa_2Se_4$	1.155	1.240	1.350

tion in the temperature range 250 to 350° C. This shows that the extrinsic defects are indeed very small in these crystals.

Simultaneously, we studied the variation of thermoelectric power with temperature over the same temperature range. All compositions exhibited n-type conduction. In the first heating cycle, the thermoelectric power was found to decrease from $\sim 400 \mu V\,°C^{-1}$ to $300 \mu V\,°C^{-1}$. In the second and third cycles the thermoelectric power shows a marked increase with temperature Figs. 8 to 12. The small values of thermoelectric power indicate that the samples are intrinsic in the first cycle whereas the negative sign may probably be attributed to the higher mobility of electrons than of holes.

The variation of activation and thermoelectric power may be attributed to two factors: (1) loss of S or Se giving the crystals excess electrons, and (2) diffusion of In or Ga giving crystals an excess of metal. Both these factors would increase with temperature and time. The first heating cycle may, therefore, be assumed to give the effects of the intrinsic conduction, whereas the second and third cycles give the effects, in addition to the intrinsic, of the loss of S and Se and diffusion of In and Ga.

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