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# Thermally stimulated conductivities in $CdInGaS_4$

Takeo Takizawa, Jun-ichi Fujii and Shigetaka Nomura
Department of Physics, College of Humanities and Sciences, Nihon University, Setagayaku, Tokyo 156, Japan

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**Abstract.** To investigate the characteristics of traps in a single crystal of $CdInGaS_4$, the thermally stimulated current has been measured in the temperature range from 90 to 300 K by varying the wavelength of light used for excitation.

The results are analysed in terms of the discrete-level model first developed by Haering and Adams. On the basis of the slow-retrapping regime, least-squares curve fittings are made to distinguish between trapping levels. Trap energies are obtained as 0.13, 0.15, 0.17 and 0.21 eV for shallow traps and 0.3 eV for deep traps together with other trapping parameters. From the value of the cross sections obtained, all the traps are considered to be associated with repulsive centres.

## 1. Introduction

A single crystal of $CdInGaS_4$ is known to be a layered semiconductor (Shand 1970) occupying a central place in the pseudo-binary system consisting of $CdIn_2S_4$ (spinel) and $CdGa_2S_4$ (defect chalcopyrite). It shows photoconduction (Abdullaev *et al* 1974, 1975, Irie *et al* 1983, Charbonneau *et al* 1985, Takizawa *et al* 1988) which is persistent for orders of minutes at low temperatures after excitation by light has ceased. Such a long persistency of photoconduction shows that this crystal has many electron traps, presumably on account of its large amount of structural defects inevitably introduced during crystal growth. These defects also have a strong influence on the electrical and optical properties of these materials.

Thus, the study of the mechanisms of these defects is very important not only in designing or controlling these materials but also in investigating the defect physics in the crystal formation of these multinary compounds.

A thermally stimulated current (TSC) is a well known phenomenon in such materials which contain many carrier traps with a long lifetime and is one of the best methods of revealing the mechanisms of the electron traps (Chen and Kirsh 1981, Takizawa and Kanbara 1986). Abdullaev *et al* (1977) have already measured the TSC in $CdInGaS_4$. However, their TSC data seem to contain some spurious signals probably owing to unfixed electrical contacts occurring during the rapid heating cycle usually adopted in this method. The abnormal behaviour of the TSC was also observed in our experiments when good contact between the sample and electrodes was not obtained.

In this report, we present the TSC results obtained using good-quality samples which consist of a single phase and do not show green emission when excited by band-edge

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light (Endo *et al* 1990, Irie *et al* 1987) together with a well prepared sample holder under various wavelengths of excitation light around the absorption edge; we also discuss the trapping characteristics as well as the distribution of the electrons captured in the trapping levels.

## 2. Experimental and analytical procedures

### *2.1. Experimental procedure*

Single crystals of $CdInGaS_4$ were made by the normal freezing method (Endo *et al* 1990) from a melt of the stoichiometric composition of 99.9999% pure elements. Samples were peeled into laminae of about 3 mm × 5 mm × 0.1 mm size. A typical resistivity is higher than $10^8$ Ω cm in the dark at room temperature.

The temperature of the sample is varied from 90 to about 300 K using a holder attached to a heating device as shown schematically in figure 1. Care is taken to remove the stress due to thermal expansion during the heating cycle. The sample is illuminated by light from a 250 W halogen lamp through a 1 m grating monochromator (1200 grooves $mm^{-1}$, blazed at 500 nm). The system of the measurements is almost the same as that in a previous paper (Takizawa and Kanbara 1986).

### *2.2. Analytical procedure*

For the TSC of *n*-type semiconductors, the observed currents arise mainly from conduction electrons released from traps. In a simple two-level system, the following rate equations hold by taking the electron lifetime and the rate of retrapping into account (Haering and Adams 1960):

$$dn_i/dt = -n_i N_c S v \exp(-E/kT) + n_c(N_i - n_i)Sv \tag{1}$$

$$dn_c/dt = -n_c/\tau - dn_i/dt \tag{2}$$

where $n_c$ is the concentration of conduction electrons, $n_i$ the concentration of trapped electrons, $N_c$ the density of states for the conduction band edge, $N_i$ the density of states of the trapping states, $S$ the capture cross section for traps, $v$ the mean thermal velocity of conduction electrons, $\tau$ the mean lifetime of the electrons and $E$ the trap depth.

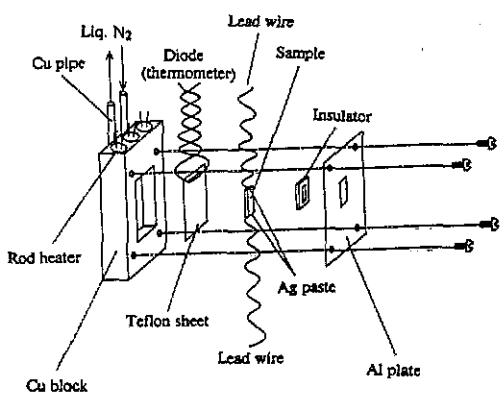


**Figure 1.** A schematic diagram of the sample holder.

In equation (1), the first term represents the number of electrons escaping from traps per unit time and is inversely proportional to the time within which electrons in traps are all exhausted when the sample temperature is fixed at an appropriate value. This time is estimated as less than $10 \times 10^{-3}$ s by measuring the decay time of photocurrent after illumination by a square light pulse at room temperature and by assuming the value $E$ as about 0.1 eV.

On the other hand, the second term represents the number of electrons retrapped from the conduction band and is inversely related to the time during which almost all traps may capture electrons. This is estimated as about 10 min from the illumination time when a peak of the TSC is saturated to reach its maximum.

Accordingly, the second term can be neglected in equation (1). This situation just corresponds to the slow-retrapping regime of Haering and Adams (1960). Then, the number of trapped electrons at $T$ are given by the following relation:

$$n_t = n_0 \exp\left[-\frac{1}{\beta}\int_{T_0}^{T} N_c S v \exp\left(-\frac{E}{kT}\right) \mathrm{d}T\right] \tag{3}$$

where $\beta$ is the heating speed and $T_0$ is the lowest temperature for a sample.

The lifetime $\tau$ in equation (2) is not identical with the decay time of luminescence but is considered to be very close to it. By using a pulsed light of an $N_2$ laser and measuring the decay of luminescence, the time is estimated as less than 1 $\mu$s. Thus, the change $\mathrm{d}n_c/\mathrm{d}t$ in photoconductivity is three orders of magnitude smaller than $n_c/\tau$, so that the following relation holds:

$$n_c = -\beta\tau(\mathrm{d}n_t/\mathrm{d}T). \tag{4}$$

Since conductivity is defined as $n_c e\mu$ where $e$ is the charge of an electron and $\mu$ the mobility, the following equation is derived if $\mu$ is assumed to be constant over the temperature range where the TSC is observed:

$$\sigma(T) = A \exp[\![ -E/kT - \{[(E/kT_m)^3/(E/kT_m + 2)] \exp(E/kT_m)\} \times (E/kT)^{-2} \exp(-E/kT)]\!] \tag{5}$$

where $A$ is the constant determined by the initial population of electrons in traps and $T_m$ is the temperature where the TSC takes its maximum value. In deriving equation (5), $E > kT_m$ is assumed.

The attempt-to-escape frequency $\nu$ which is a measure of how frequently electrons try to escape from traps is determined as follows:

$$\nu = N_c S v = (k\beta/E)(E/kT_m)^2 \exp(E/kT_m) \tag{6}$$

where

$$N_c = 2(2\pi m^* kT)^{3/2}/h^3 \qquad v = \sqrt{3kT/m^*}$$

and $m^*$ is the effective mass of a conduction electron. Then the capture cross section $S$ is derived as

$$S = \nu/N_c v = [h^3/2m^*(kT)^2\sqrt{3(2\pi)^3}]\nu \tag{7}$$

that is

$$S = [1/3 \times 10^{26}(T/300)^2](\nu/\hat{m}) \tag{8}$$

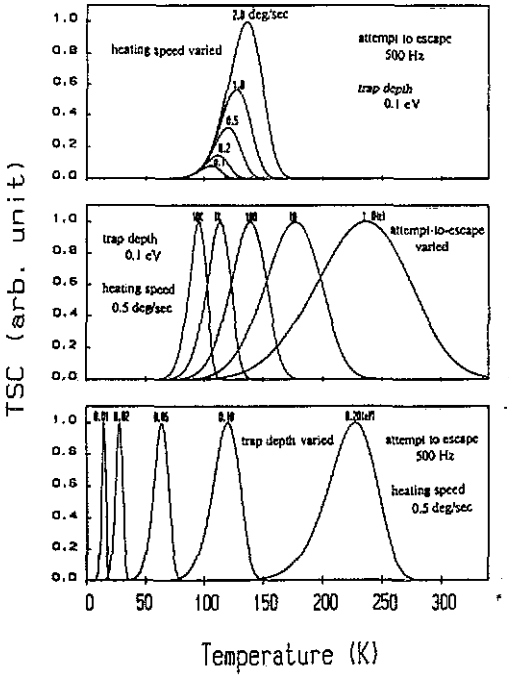


**Figure 2.** Examples of calculations by equation (5) in the text: top panel: the heating speed $\beta$ is varied while the trap depth $E$ and the attempt-to-escape frequency $\nu$ are kept constant; centre panel: $\nu$ is varied while $E$ and $\beta$ are kept constant; bottom panel: $E$ is varied while $\nu$ and $\beta$ are kept constant. All the curves are normalized to unity except in the top panel where the curves are normalized by the peak value at $\beta = 2.0\ \mathrm{K\,s^{-1}}$.

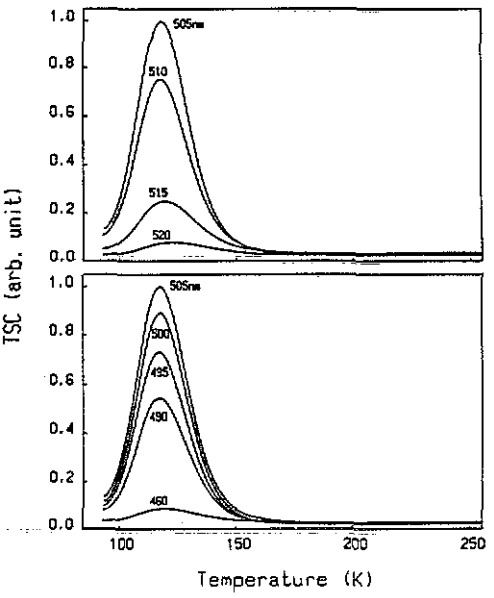


**Figure 3.** TSC curves excited by light having different wavelengths. The heating speed is $0.5\ \mathrm{K\,s^{-1}}$.

where $\hat{m}$ is the specific mass ratio to the free-electron mass. Examples of lineshapes calculated by equation (5) are summarized in figure 2.

Using equation (5), we can decompose the measured curve into a series of single TSC curves making use of the least-squares method, where $A$, $E$ and $T_m$ are taken as unknown parameters. These three parameters are changed independently for each TSC so that the deviation between observed and calculated curves would give the minimum value.

## 3. Results and discussion

The TSC results for $CdInGaS_4$ excited by light having several different wavelengths are shown in figure 3 where the heating speed is set at a constant value of $0.5\ \mathrm{K\,s^{-1}}$ throughout the experiments. The intensity of the illumination on the samples is also kept nearly constant over the wavelength range investigated.

It is seen in figure 3 that the intensity of the TSC spectra markedly depends on the wavelength of light for excitation. The intensity has a maximum at 505 nm (2.46 eV) which is just below the indirect absorption edge already obtained as 2.56 eV (484 nm)

at 90 K (Tarricone and Lottici 1987). The peak in the TSC spectra shifts to high temperatures as the wavelength of illumination increases to more than 510 nm and stays nearly constant for wavelengths less than this value. From these facts, it is shown that the pumping of electrons into trapping levels occurs in resonance with the band-gap energy, and that the population of electrons changes according to the photon energy of excitation.

The trapping levels arise from defects which are inevitably introduced during crystal formation, and several kinds of level may exist according to the types of defect. These defects are distributed randomly in space not too close to each other, so that the trapping levels are expected not to be spread widely in energy and can be seen as isolated levels with a finite energy width.

As stated in the previous section, each TSC curve can be decomposed into several independent components by use of equation (5), if the trapping levels are discrete and isolated from each other. We made the decomposition on the basis of this assumption.

In the process of the decomposition, we first consider only one trapping level to fit the observed curve using the least-squares method. If there is a discrepancy of more than $10^{-4}$ of the standard deviation in the fitting, we add another level to obtain a better fit. If this again gives an unsatisfactory result, we shall add a third level. We continue this process until a good fit is obtained. This decomposition may not be unique but it is surely the one which contains the least number of trapping levels. The results of this decomposition are shown in figures 4 and 5, where the peak TSC is normalized to unity.

Four kinds of trap which we call trap $i$ ($i = 1, 2, 3, 4$) emerge from this procedure. Their trap depths are shown in figure 6, and the trapping parameters are summarized in table 1. These values have been determined within an error of a few per cent when the experiment was repeated using the same sample, giving TSC curves similar to each other observed under different experiments. However, the trap depths and other parameters differ by about 10% from sample to sample even when the sample was cut from the same ingot. We suspect that this might be due to the difference between the electrical contacts arising in the sample manipulation in addition to the difference between the characteristics of the samples themselves. In the following, we use only the results obtained for a typical sample, but we believe that the general feature of the trapping characteristics will not be lost.

The number of electrons captured in each trap can be estimated from the area below each decomposed TSC spectrum. The electron distribution map thus obtained is shown in figure 7. The right-hand side of figure 7 represents the total number of electrons released from all the traps when excited by the respective light indicated. The number is a maximum at 2.46 eV (505 nm), gradually decreases above this energy and rapidly decreases below this energy.

As shown in figure 6, the trap depths are well defined between 490 and 510 nm. However, trap 1 and trap 2 shift to deeper levels as the wavelength becomes longer. This can be explained if the finite width of the trapping level is taken into account.

In the process of the above decomposition, trapping levels without a linewidth are assumed so that the depth of a trap should be determined uniquely. However, the actual trap which we call the 'trap $i$ ($i = 1$–4)' consists of many defects having similar characteristics and weakly interacting with each other. Thus, the deduced value for a trap depth through the fitting is considered to be a mean value of the depths for the trapping levels occupied by the actual population of electrons in the sample.

Trap 1 and trap 2 are filled with more electrons when excited with light of 490–510 nm than when excited with light having a wavelength outside this range as shown in figure

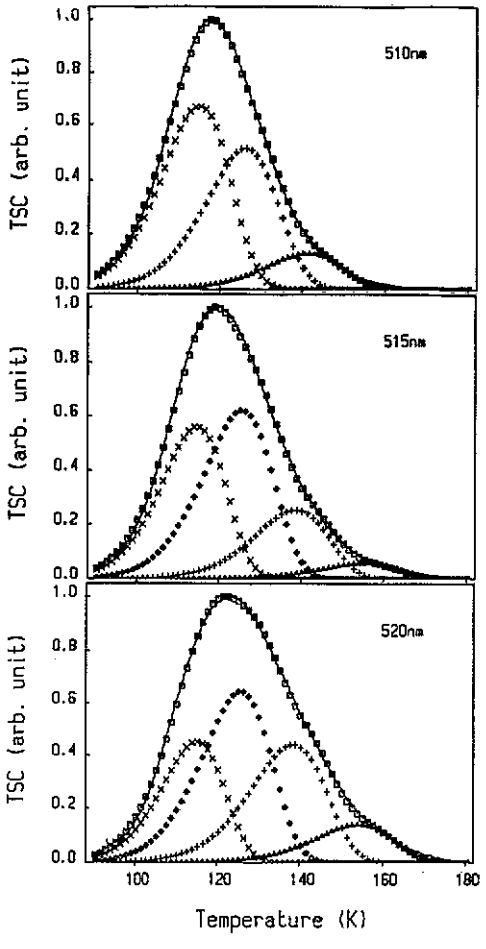


**Figure 4.** Decompositions of TSC curves for 460, 490 and 505 nm illuminations into a number of discrete traps by the use of the least-squares method: ×, +, ◇, decomposed curves; □, sum total of decomposed curves; ———, experimental results.

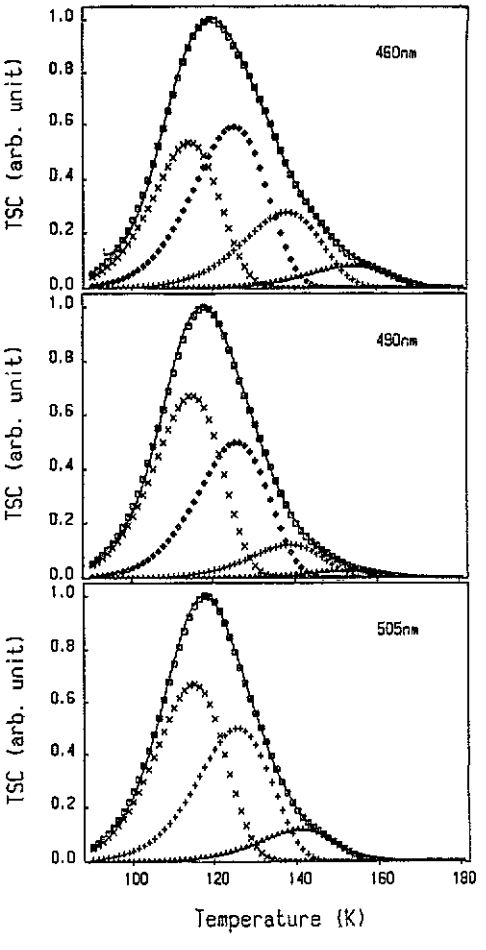


**Figure 5.** Decompositions of TSC curves for 510, 515 and 520 nm illuminations in the same manner as in figure 4.

7. If electrons are filled from the deepest levels which exist within the photon energy range with respect to the top of the valence band, the trap depth will be observed to be deeper in the case of lower population of electrons. This explains the shift of the trap depth at wavelengths longer than 510 nm in figure 6.

On the contrary, if the sample is illuminated by light having a higher energy than the band edge, the excited electrons will be relaxed by losing their kinetic energy to become trapped in randomly distributed defect levels. In this case, electrons are equally distributed in trapping levels with a little higher trapping probabilities in shallower levels than in deeper levels. The trap depths observed at wavelengths below 505 nm in figure 6 correspond to this situation.

**Table 1.** Trap parameters for $CdInGaS_4$: $E$, the trap depth; $T_m$, the maximum temperature; $\nu$, the attempt-to-escape frequency; $S$, the capture cross section.

| Trap | $E$ (eV) | $T_m$ (K) | $\nu$ ($\times 10^4$ Hz) | $S$ ($\times 10^{-22}$ cm$^2$) |
|---|---|---|---|---|
| 1 | 0.125 | 115 | 2 | 4.5 |
| 2 | 0.145 | 125 | 5 | 9.6 |
| 3 | 0.17 | 139 | 10 | 15.5 |
| 4 | 0.21 | 154 | 40 | 50.6 |

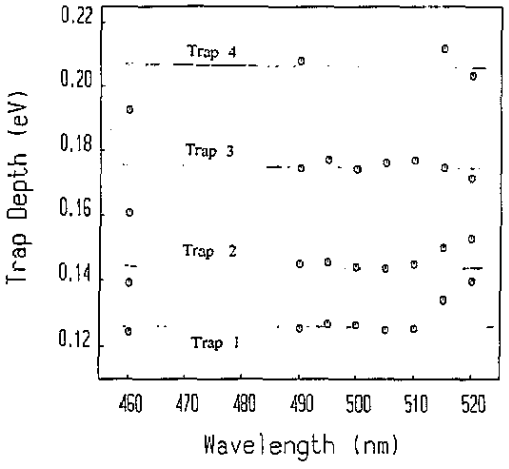


**Figure 6.** Trap depths as a function of the wavelength of light for excitation, obtained from the fitting procedure shown in figures 4 and 5: ———, guides for the eye.

In figure 8(*a*) other TSC spectra are shown, which were obtained by illuminating under a constant temperature of 200 K followed by cooling in the dark to 90 K and by again heating to room temperature. The effect of illumination appears above 200 K and depends also on the wavelength of light. To see the effect more clearly, we calculated the spectra by subtracting the TSC curve at 460 nm where little structure is found.

A structure which could not be observed in the normal TSC as shown in figure 3 emerges (see figure 8(*b*)). This structure has its maximum at 520 nm and becomes smaller as the wavelength of illumination increases, finally disappearing above 560 nm. It appears only when a sample is illuminated in a thermal reservoir of 200 K and can be ascribed to a deep level surrounded with a barrier. The level is filled only with electrons having sufficient kinetic energy to jump over the barrier. This kind of level has also been observed in CdS and $CdIn_2S_4$ and has been ascribed to a trap with a repulsive potential (Bube *et al* 1966, Takizawa and Kanbara 1986). From the shape analysis, the depth is estimated as about 0.3 eV.

From the fundamental concept of traps (Milnes 1973), it is said that a cross section ranging from $10^{-12}$ to $10^{-15}$ is due to attractive centres, a cross section from $10^{-15}$ to $10^{-17}$ is usually ascribed to neutral centres, and a cross section of the order of $10^{-22}$ is associated with repulsive centres. The cross section of traps in our experiment shown in table 1 is as small as that of repulsive centres. As mentioned above, the deep trap of 0.3 eV also

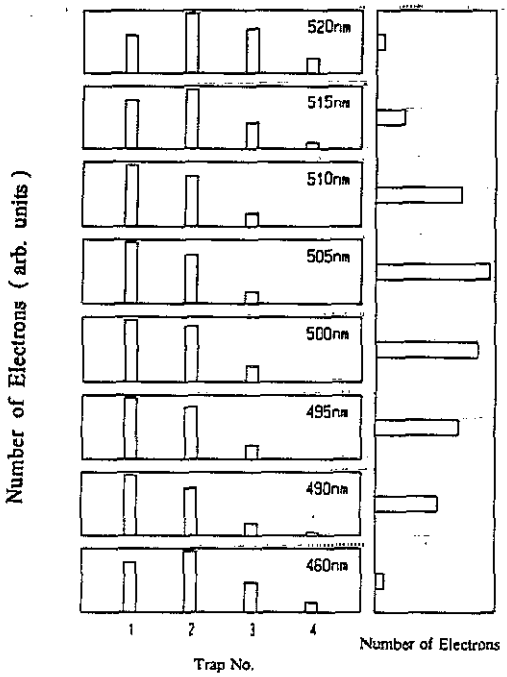


**Figure 7.** The distribution map of electrons in traps excited by light having various wavelengths, obtained from areas below the decomposed curves shown in figures 4 and 5. In the diagram on the right, the total electrons trapped in the crystal are shown as a function of wavelength of the exciting light. The histograms on the left show the distributions of electrons in different traps for different wavelengths. The height in each histogram is normalized to the maximum number of electrons in each excitation.

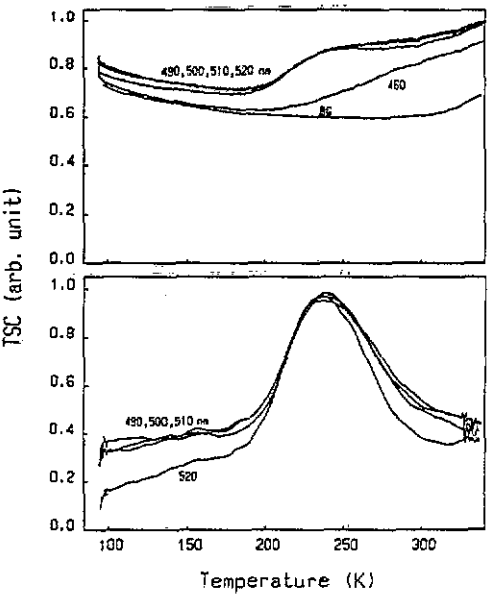


**Figure 8.** Upper: TSC curves measured with illumination under 200 K followed by cooling to 90 K. The symbol BG represents the TSC curve taken in the dark, without illumination. Lower: TSC curves with the 460 nm curve subtracted as a background spectrum.

has a repulsive barrier around itself, so that all the traps in the $CdInGaS_4$ single crystal are considered to be associated with repulsive centres.

As a candidate for the shallowest trap 1, sulphur vacancies are suggested, because the TSC signal of trap 1 changes drastically when the sample heated above 400 K is used, where the resistivity of the sample is decreased owing to a little separation of sulphur from inside the sample. Candidates for other traps may be Ga or In defects (Matsushita *et al* 1990), or imperfections due to the exchange of cations in the crystal lattice. A detailed study of the origins of these traps is now in progress using electron paramagnetic resonance and will be published in the near future.

## 4. Summary

The TSC in a $CdInGaS_4$ single crystal was measured in the temperature range from 90 to 300 K by changing the wavelength of light.

The results were analysed in terms of the discrete-level model, first developed by Haering and Adams. On the basis of the slow-retrapping regime, several trapping levels were revealed by using the least-squares curve fitting. Trap energies were obtained as 0.13, 0.15, 0.17 and 0.21 eV for shallow traps and 0.3 eV for deep traps together with other trapping parameters. From the value of the small cross sections of shallow traps in addition to the fact that the deep trap of 0.3 eV has a repulsive potential barrier, all the traps in $CdInGaS_4$ can be said to be associated with repulsive centres.

## Acknowledgment

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