JOURNAL OF MATERIALS SCIENCE 4 (1969) 570–573

On the Thermoelectric Properties of $Cd_xHg_{1-x}Se$ Alloys

E. CRUCEANU, S. IONESCU-BUJOR
Institute of Physics, Academy of the Socialist Republic of Romania, Caleà Victoriei, Bucharest, Romania

Received 7 January 1969

The thermal and electrical conductivity, Hall and Seebeck coefficients have been measured as a function of temperature for various undoped alloys up to $x = 0.50$. The Hall coefficient and the thermoelectric power remained negative for all samples at all temperatures in the investigated range (77 to 450° K).

The alloys with $x = 0.10$ provided the optimum figure of merit, which reached a maximum of 0.9×10^{-3} deg^{-1} at 400° K. This represents an improvement of at least 50% over the best values for n-type Ge–Si alloys below 700° K.

1. Introduction

Recent developments in the theory and design of multistage thermoelectric generators have made necessary the study of materials with a high figure of merit $Z = \alpha^2\sigma/K$, at relatively low or intermediate temperatures. A little-studied alloy system which, according to its basic component properties, should present compositions characterised by high values of the figure of merit is the $Cd_xHg_{1-x}Se$ alloy system. The high electrical conductivity σ of HgSe, coupled with a very low lattice thermal conductivity [1, 2] would be expected to yield valuable properties to solid solutions with CdSe, suiting them for use as materials for thermoelectric generators at temperatures up to 400 to 450° K. Also suitable would be the high thermoelectric power α, shown by CdSe, and its low total thermal conductivity K, of only 0.0434 W/cm °K [3].

The present paper is concerned with data on the electrical and thermal properties of $Cd_xHg_{1-x}Se$ alloys with compositions near to HgSe, as well as with bringing into relief some thermoelectric characteristics for further use. The study has been limited to the compositions with x below 0.5 and with no controlled doping. The influence of annealing under Hg, Cd or Se vapour on the electrical and thermal properties of the alloys was not investigated.

2. Preparation and Structural Properties of the Alloys

The possibility of forming solid solutions within the entire range of compositions has already been shown [4, 5]. The presence of the same anion in both lattices and the equality of the cationic tetrahedral covalent radii favour the formation of homogeneous solid solutions, regardless of whether one starts from the basic elements – Hg, Cd, Se – or from the HgSe and CdSe compounds, previously synthesized. In the present work HgSe and CdSe were prepared from highly purified elements: Cd, Se–99.9999% and Hg distilled four times. The solid solutions were synthesized in quartz ampoules – previously sealed under vacuum, which were held at a constant temperature about 50° C under the solidus curve for 50 h. After carrying out the synthesis massive homogeneous polycrystalline ingots were obtained by the Bridgman method. X-ray diffraction analysis, using the Debye-Scherer method, showed that all compositions had a zinc-blende structure. Using metallographic analyses all samples showed the presence of a single phase only.

All solid solutions in this system have unstable electrical and thermal properties at temperatures above 500° K, especially for an x value below 0.25. This fact set a limit on the study of these alloys as a function of temperature under normal pressure.

3. Experimental, Results and Discussion

The Hall effect, the thermoelectric power and the thermal and electrical conductivity measurements were carried out on compositions with $x = 0$; 0.03; 0.06; 0.10; 0.25; 0.50.

At temperatures above 500° K some irreversible effects were observed so the upper measurement temperature was restricted to 450°K. Below this temperature all experimental data were reproducible within the estimated error of measurement. The curves in figs. 1, 2, 3 and 5 which show the variation of different parameters as a function of temperature are numbered in order of increasing x as follows: 0 refers to $x = 0.00$; 1 refers to $x = 0.03$; 2 refers to $x = 0.06$; 3 refers to $x = 0.10$; 4 refers to $x = 0.25$; 5 refers to $x = 0.50$.

3.1. Electrical Properties

Figs. 1 and 2 represent the variation of the Hall coefficient and the electrical conductivity as a function of temperature for the above mentioned compositions. Assuming that the Hall constant, $R_H = 1/en$, it can be seen from fig. 1 that the alloys with an x below 0.25 all have approximately the same electron concentration, n, in the conduction band. This furthers the comparison between the electrical and thermal characteristics of the alloys within this range of alloy composition. The electron concentration for $0 \leqslant x \leqslant 0.25$ varies between 1.7×10^{18} cm^{-3} and 9×10^{17} cm^{-3}, respectively.

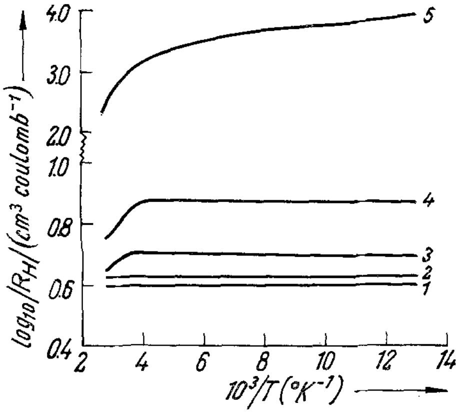

Figure 1 The Hall coefficient versus $1/T$.

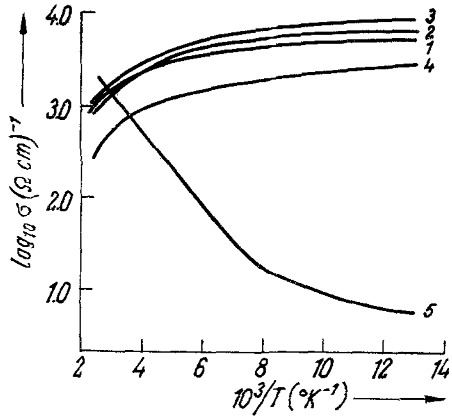

Figure 2 The electrical conductivity versus $1/T$.

As can be seen from the variation of the electrical conductivity with the temperature, the electrical behaviour of these alloys points to their semi-metallic character. The product $|R_H\sigma|$ (fig. 3) shows very high values and throughout the temperature range observed, a monotonic decrease with increasing temperature. The variation of $|R_H \sigma|$ with temperature for $T > 300°$ K is of the form T^{-r}, where r ranges between 1.5 and 2. This points to a combination of charge carrier scattering by accoustical and optical phonons [6, 7] the former scattering mechanism nevertheless prevailing.

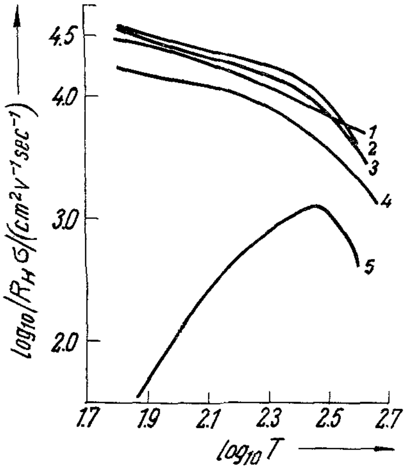

Figure 3 The Hall mobility versus $1/T$.

Fig. 4 shows the Hall mobility at 77 and 300° K as a function of the alloy composition for x between 0 and 0.30. It has to be mentioned that with this system of solid solutions as well as with the HgTe – CdTe and HgTe – ZnTe [8, 9] there occurs a mobility maximum near the compound with the greatest mobility of electrons (HgSe or

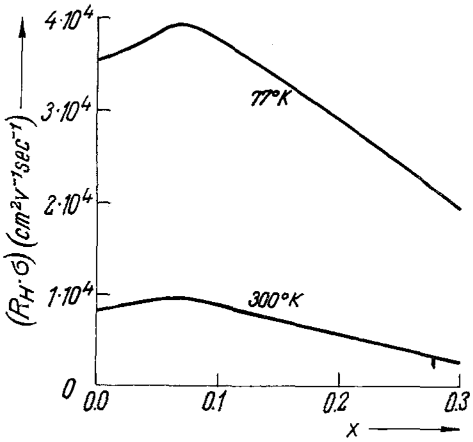

Figure 4 The Hall mobility as a function of composition near HgSe.

HgTe). In the present case the maximum is attained at a value of x about 0.10 and becomes much more conspicuous at lower temperatures (77° K) rather than at 300° K. This agrees with the earlier hypothesis [8] concerning the CdTe–HgTe system, which shows many similarities to the present alloy system.

Taking into account the conclusions reached in [8, 9] it is reasonable to suppose that thermal treatments under vapour pressure could significantly increase the mobility and electrical conductivity values of our alloys, and this might entail an increase of the figure of merit.

3.2. Thermoelectric Properties

Figs. 5 and 6 show the variation of the thermoelectric power as a function of temperature and composition, respectively. A monotonic increase of the thermoelectric power in both cases can be accounted for by the semi-metallic nature of the alloys with an x below 0.25 and by an increase of the effective mass of the electrons when departing from HgSe.

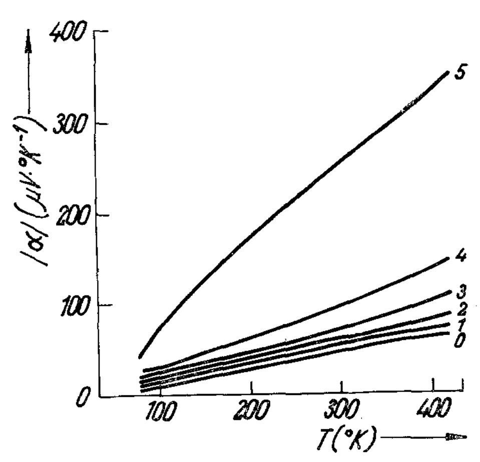

Figure 5 The Seebeck coefficient versus $1/T$.

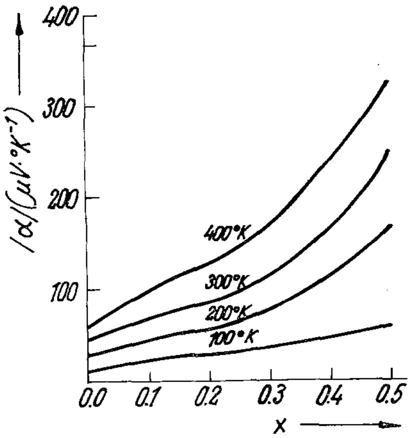

Figure 6 The Seebeck coefficient as a function of composition.

Since the degree of degeneration of the electronic gas in our samples was not high enough—$E_{F/KT}$ less than 4—and the relaxation time could not be satisfactorily estimated even at higher temperatures, it was not possible to calculate the electron effective mass from the Seebeck coefficient.

3.3. Thermal Conductivity and the Figure of Merit

Using the same method as reported in [2] and

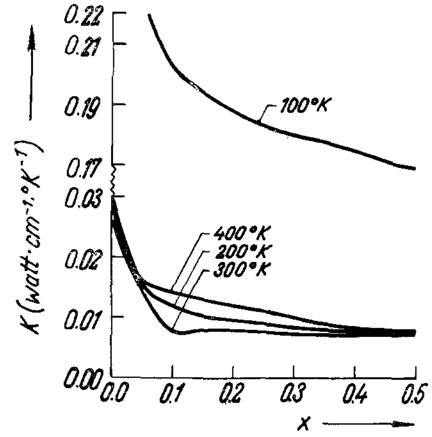

Figure 7 The thermal conductivity as a function of composition at 100, 200, 300 and 400° K.

[10] the total thermal conductivity K was calculated from the thermal diffusivity measurements. Fig. 7 shows the variation of this parameter as a function of the alloy composition at four temperatures. No attempt was made to separate the electronic part from the total thermal conductivity since the objective was restricted to the possibility of calculating the figure of merit Z, as defined in section 1.

Fig. 8 shows the results concerning the figure of merit of the $Cd_xHg_{1-x}Se$ alloys. It has to be mentioned that at temperatures between 300 and 400° K the alloys with an x about 0.10 display figure of merit values comparable with (or even higher than) those of some n-type solid solutions of III–V covalent compounds, which in their turn are superior to the Ge–Si alloys [10]. The figure of merit obtained for the compositions with $x = 0.10$ can be improved provided the alloys are, as mentioned above, submitted to some optimal annealing under vapour pressure, or to some suitable dopings.

4. Conclusions

It can be seen from the preliminary data on electrical, thermal and thermoelectrical properties of $Cd_xHg_{1-x}Se$ alloys that the system presents for n-type materials some figures of merit comparable, within the 400 to 450° K range, to those of the best thermogenerator materials. The properties resulting from the high electron mobility in alloys with an x of about 0.10 can also point to further uses.

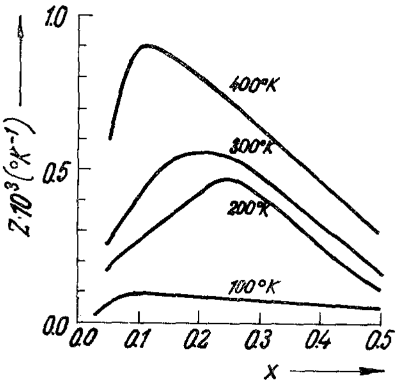

Figure 8 The figure of merit as a function of composition at 100, 200, 300, and 400° K.

References

1. CH. WHITSETT, *Phys. Rev.* **138** (1965) 829.
2. F. KELEMEN, A. NEDA, E. CRUCEANU, and D. NICULESCU, *Phys. Stat. Sol.* **11** (1965) 865.
3. A. D. STUCKES and G. FARREL, *J. Phys. Chem. Solids* **25** (1964) 477.
4. M. V. KOT and V. A. MSENSKI, *Izvestia ANSSSR-Fiz.* **28** (1964) 1069.
5. E. CRUCEANU and D. NICULESCU, *C.R. Acad. Sci. Paris* **261** (1965) 935.
6. M. SCHNEIDER, *C.R. Acad. Sci. Paris* **264B** (1967), 70.
7. L. L. KORENBLIT, S. A. ALIEV, and S. S. SALÎT, *Fiz. Tverd. Tela* **7** (1965) 1673.
8. HUGUETTE RODOT, thesis, University of Paris, 1964.
9. E. CRUCEANU, D. NICULESCU, N. NISTOR, and S. IONESCU-BUJOR, *Fiz. Tverd. Tela* **7** (1965) 2039.
10. I. KUDMAN, L. EKSTROM, and T. SEIDEL, *J. Appl. Phys.* **38** (1967) 4641.