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PHONONS-DEFECTS INTERACTIONS IN CdTe

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Résumé. — Les défauts électriquement inactifs dans CdTe ont été mis en évidence par deux méthodes :

- conductivité thermique à basse température,
- topographie X.

Dans tous les matériaux étudiés, créés par T. H. M. ou fusion de zone, non dopés, dopés au chlore et à l'indium, des microprécipités ont pu être étudiés. Leur concentration, déduite des mesures de conductivité thermique par un calcul basé sur la méthode de Callaway, est comprise entre 10^{14} et 10^{15} cm⁻³ et leur diamètre moyen supérieur ou égal à 100 Å. Cette concentration est indépendante du taux de dopage et de la méthode d'élaboration. Des précipités beaucoup plus grands (1 µm) apparaissent en topographie X sur les cristaux non dopés et purifiés par fusion de zone ainsi que sur les matériaux dopés au chlore. Il n'y a pas de corrélation entre ces défauts et les microprécipités.

Abstract. — A study of electrically inactive defects has been performed on CdTe single crystals by two different experimental techniques :

- the low temperature thermal conductivity measurement. It has been used as a tool to study crystal defects, such as clusters, stacking faults or point defects ;
- the X ray topography. It completes the first method in showing large aggregates (resolution $\simeq 1$ µm), dislocation arrays or structural defects.

The following observations regarding the experimental results are worth noting. CdTe crystals (undoped, Cl or In doped) have been grown by melting zone or THM. Microprecipitates are found in all CdTe crystals. The concentration varies from 10^{14} up to 10^{15} cm⁻³ and the mean diameter reaches 100 Å or more. This concentration is independent on the doping level and on the crystal growth process. The presence of such a precipitation is probably associated with the chemical and thermal growth conditions of the crystals. The $K(T)$ curves fit by the Callaway phenomenological model indicates a point defect concentration of about 10^{18} cm⁻³. The isotopical mass deviation introduces only a concentration of 7×10^{17} cm⁻³. The excess is ascribed to several origins such as nonstoichiometry in CdTe, doping, chemical impurities or V_{Cd} . In X-ray topography large precipitates appear only in crystals not intentionally doped and melting zone purified, or in CdTe : Cl. No correlation is found between large and micro precipitates. Dislocations with atmosphere appear also with a low concentration of about 10^4 cm⁻².

1. Introduction. — The study of the thermal conductivity of CdTe at low temperature has been pursued by different authors as Holland [1] and Slack [2, 3]. Slack analyses the influence of phonon scattering by magnetic impurities on thermal conductivity. On the other hand, electrical measurement results show a strong correlation between electrical properties and elaboration methods. In order to find or not such a correlation with nonactive electrical defects, we have measured the thermal conductivity of different specimens produced by :

- vertical zone melting technique,
- modified Bridgmann technique,
- Travel Heater Method (T. H. M.).

The interpretation of our experimental results is made with the Callaway phenomenological model.

2. Experiments. — The experimental apparatus of thermal conductivity measurements was described in several publications [4, 5, 6]. It is a comparative method which allows the use of small dimension samples.

The measurements are performed between 1.4 K to 300 K, the relative incertitude is about 1 % to 3 % for temperature and lower than 10 % for thermal conductivity. Our samples are separated in two groups :

- the first group concerns specimens the elaboration of which involves fusion of the material,
- the elaboration of specimens of the second group is performed at a temperature lower than the melting point of CdTe.

Experimental results are shown figure 1 (first group) and figure 2 (second group). The curves for all the specimens are comparable, they show a maxi-

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FIG. 1. — Thermal conductivity of first group samples.

FIG. 2. — Thermal conductivity of second group samples.

imum value of thermal conductivity of $1.5 \text{ W.cm}^{-1} \text{ K}^{-1}$ to $3 \text{ W.cm}^{-1} \text{ K}^{-1}$ at a temperature of about 14 K to 17 K. The thermal conductivity becomes proportionnal to T^3 under 2 K. In the figures, the solid lines are the Callaway model fits.

3. Analysis. — **3.1 MODEL.** — We have carried out a quantitative analysis of our thermal conductivity data with the Callaway model [7] which is now well established by many investigators such as Nettleton [8] and Berman and Brock [9]. This model uses a Debye spectrum as dispersion curve and involves also the additivity of the inverse of independant relaxation times. A difficulty in the theoretical analysis of thermal conductivity is the determination of the relaxation times τ of the respective phonon scattering processes. The total relaxation rate τ_{tot} used in the Callaway formalism is :

$$\tau_{\text{tot}}^{-1} = \sum_{i=1}^n \tau_i^{-1}. \quad (1)$$

Phonon scattering processes are well known and we consider consecutively :

3.1.1 Boundary phonon scattering

$$\tau_1^{-1} = \frac{v}{L'} \quad (2)$$

when L' is Casimir's length. For samples of square cross section $L' = 1.12(l_1 \cdot l_2)^{1/2}$, l_1 and l_2 are lateral dimensions. v : mean sound velocity.

3.1.2 Phonon scattering by point defects. — The phonon scattering cross section of point defects can be calculated from Klemens' formula [10] :

$$\tau_2^{-1} = A\omega^4 \quad (3)$$

where

$$A = \frac{3 V_0 \Gamma}{\pi v^3} \quad (4)$$

V_0 : volume of elementary cell,

Γ : point defect scattering parameter.

For an atomic impurity X , we have :

$$\Gamma(X) = C \sum_i f_i \left(\frac{m_i - m_x}{m_x} \right)^2 \quad (5)$$

where

$$m_x = \sum_i f_i m_i$$

f_i is the fractional concentration of the i -th isotope of mass m_i of the impurity X ;

C is a constant. $C = 1/12$ for X low concentration.

For a compound $X_x Y_y$, $\Gamma(X, Y)$ is given by :

$$\Gamma(X, Y) = \frac{x}{x+y} \left(\frac{m_x}{\bar{m}} \right)^2 \Gamma(X) + \frac{y}{x+y} \left(\frac{m_y}{\bar{m}} \right)^2 \Gamma(Y) \quad (7)$$

where :

$$\bar{m} = \frac{xm_x + ym_y}{x+y}. \quad (8)$$

We may consider this compound as a monoatomic material of average mass $\bar{m}$ and of unit cell average volume V , because at a temperature lower than $\theta_D/10$ all the atoms of one cell vibrate with the same phase.

3.1.3 Phonon-phonon interaction. — The Callaway model involves :

$$\tau_3^{-1} = B\omega^2 T^3 \quad (9)$$

where B : anharmonic parameter.

3.1.4 Phonon scattering by clusters. — Two limiting cases are well defined :

— if the size « a » of the spherical clusters is much smaller than the inverse of phonon momentum q , then they act as Rayleigh scatterers and the effective scattering cross section is proportional to ω^4 ,

— in the other case, where « a » is much greater than the inverse of phonon momentum, the effective scattering cross section will be independant of the

phonon frequency and proportional to the geometrical cross-section :

$$\tau_4^{-1} = \frac{1}{4} S \pi \frac{a^6 \omega^4}{v^3} \quad (\text{for } qa \ll 1) \quad (10)$$

$$\tau_4^{-1} = \frac{1}{4} S \pi a^2 v \quad (\text{for } qa \gg 1) . \quad (11)$$

FIG. 3. — Influence of precipitate concentration on thermal conductivity of CdTe (Theoretical curve calculated with Callaway model).

FIG. 4. — Influence of precipitate diameter on thermal conductivity of CdTe (Theoretical curve calculated with Callaway model).

The different temperature dependences of such scattering processes allow to fit theoretical curves with the experimental data. The determination of the anharmonic parameter B , which is constant for a given material, is performed by fitting the thermal conductivity data of a pure specimen at a temperature of about 40 K-50 K.

We have drawn calculated thermal conductivity curves showing the successive contributions of the different parameters :

- precipitate concentration (Fig. 3),
- diameter of spherical precipitates (Fig. 4).

In these figures, the parameters A , B and L' were kept constant.

3.2 FITTING DATA. — Table I summarizes all the geometrical characteristics and fitting values of the samples of both groups. The fitting of the experimental results with Callaway's model leads to a large point defect concentration always higher than 10^{18} cm^{-3} . Only the purest samples of each group result in a lower one. The experimental data show also the existence of microprecipitates in all the specimens whatever their elaboration techniques are. The microprecipitates have a diameter of about 100 Å or more, and a concentration which can vary from $7 \times 10^{13} \text{ cm}^{-3}$ (sample 39.3) to $1.8 \times 10^{14} \text{ cm}^{-3}$ (sample 70.1).

4. Discussion. — **4.1 POINT DEFECTS.** — Cadmium and Tellurium which have many isotopes can explain a part of the high point defect concentration. Using equations [5] and [7] the calculation of the point defect parameter gives : $\Gamma(\text{Cd}) = 2.27 \times 10^{-5}$ mole fraction, $\Gamma(\text{Te}) = 2.36 \times 10^{-5}$ mole fraction, and for the compound : $\rightarrow \Gamma(\text{CdTe}) = 2.36 \times 10^{-5}$ mole fraction. The coefficient A is calculated from expression [4] : $A = 9.44 \times 10^{-44} \text{ s}^3$.

So the point defect concentration due to the isotopes of Tellurium and Cadmium is about $7 \times 10^{17} \text{ cm}^{-3}$, which can be considered as the lowest possible point defect concentration in CdTe. The higher values measured can be explained by :

- Cadmium or Tellurium vacancies ,
- impurities or doping element atoms, if they don't precipitate.

4.2 PRECIPITATES. — The chemical nature of microprecipitates cannot be determined by our method. However their presence can be related to the growth process and the thermal treatment involved in it. We know that the lack of stability at the growth interface can induce perturbation of the solid phase [1] which can lead to :

- precipitation of a second phase,
- cellular or dendritic, instead of single, crystal growth.

TABLE I

Group	N°	Elaboration	Doping parameter	Callaway model fit			Geometrical parameter			Origin
				Point defect concentration cm^{-3}	Precipitates Diameter Å	Concentration cm^{-3}	Length L cm	L/S cm^{-1}	Casimir length cm	
1	CTZ V13	Vertical zone melt.	Pure	9.4×10^{17}	108	$10^{14} \times \text{to}$ 1.5×10^{14}	0.51	5.7	0.34	A
		Idem + annealing		2.8×10^{18}	82	1.5×10^{14}	0.51	5.7	0.34	A
	CTI 79	Modified Bridgmann tech.	Indium $3 \times 10^{18} \text{ cm}^{-3}$	2×10^{18}	100	1.5×10^{14}	0.61	6.6	0.34	A
	1394 3		Indium 10^{17} cm^{-3}	1.6×10^{18}	100	1.5×10^{14}	0.68	4.5	0.44	A
	CTC 75		Chlorine $2.3 \times 10^{18} \text{ cm}^{-3}$	1.1×10^{18}	100	1.5×10^{14}	0.66	6.7	0.35	A
2	39 3	Double T. H. M.	Pure	9.4×10^{17}	100	7×10^{13}	0.71	11.3	0.28	B
	69 5	T. H. M. at 750 °C	Chlorine $2 \times 10^{18} \text{ cm}^{-3}$	8.2×10^{17}	100	10^{14}	0.69	11.1	0.28	B
	70 1		Chlorine $6.5 \times 10^{18} \text{ cm}^{-3}$	1.6×10^{18}	100	1.8×10^{14}	0.70	7.4	0.34	B
	70 2		Idem	2×10^{18}	100	1.5×10^{14}	0.73	7.8	0.35	B
	70 3		Idem	2×10^{18}	100	1.4×10^{14}	0.76	7.9	0.35	B
	1148	T. H. M. at 900 °C	Chlorine	1.1×10^{18}	100	1.5×10^{14}	0.60	6.5	0.34	C

A : C. N. R. S. Bellevue ; B : L. E. P. ; C : C. R. N. Strasbourg.

Using infrared microscopy, many investigators have reported of macroscopic ($\geq 1 \mu\text{m}$) absorbing regions in CdTe and subsequently proposed void or precipitates models related to crystal growth and post anneal conditions [12, 13]. However, the

absence of precipitates visualised by that technique does not insure that material is of high quality. X-ray reflection topography has been performed on specimens of the first group (CTZ, V 13, CTI 79, CTC 75) in order to determine the existence or not

FIG. 5. — X-rays topographies of different samples of CdTe reflexion [110], $\lambda K\alpha\text{Mo}$: 5a : sample n° CTZ V13 (magnification : 80) ; 5b : sample n° CTC 75 (magnification : 80) ; 5c : image of precipitate aggregates in CTZ V13 and CTC 75 (magnification : 300).

of such macroinhomogeneities. We can observe on these topographies (Fig. 5a and 5b) two kinds of defects :

- dislocations with a density of 10^4 cm^{-2} calculated by the Smith and Guttman method [14],
- precipitates of large diameter ($\geq 1 \mu\text{m}$) which appear on certain dislocations. At high magnification (Fig. 5c) the observations show a black spherical spot separated in two equal parts by a contrasting bright line. This can be interpreted as large precipitates or precipitates agglomerates. Such defects have been encountered in Silicon [15], Cadmium Sulphide [16] and diamond [17] for impurity precipitates.

5. Origins of precipitates. — The origin of precipitation may be extrinsic : foreign atoms whose solubility limit is exceeded at the lower temperatures, or intrinsic : retrograde solubility shape of the CdTe solidus. Both processes can also occur together.

5.1 PRECIPITATION OF FOREIGN ATOMS. — Precipitation of doping elements can be expected since data in table I show that the point defect concentration is always lower than the known quantity of doping element included in CdTe during elaboration. Only sample 1394-2 has a doping concentration of about 10^{17} Indium atoms per cm^3 and a point defect concentration of about $1.6 \times 10^{18} \text{ cm}^{-3}$. On the other hand precipitation of impurities is easy in CdTe because of the large concentration of Cadmium vacancies which allows CdTe to receive many foreign atoms. Kiseleva *and al.* [18] have found concentrations up to 10^{20} defects per cm^3 which could be Cadmium vacancies. This concentration was estimated from the difference of Te_2 vapour pressure over stoichiometric and non stoichiometric CdTe, and by microdensity measurements. We can notice these techniques are not electrical measurements. Measurements of the concentration of the different kinds of impurities were performed on specimens similar to CTZ V 13 by Triboulet *and al.* [19]. About one atomic ppm of Si, Ca, Mg, Al, Na, Cl, F, Co and Fe, were found. A large concentration of Carbon (a few tens ppm) was also found, which may come from the graphite coating of the inner surface of the synthesis quartz tube. Impurity concentrations of about 1 ppm are shown by several investigations [20, 21]. Considering the impurity segregation coefficient values in CdTe (generally ranging between 0.2 to 0.5, but more than 1 for Aluminium) and electrical measurements, Triboulet suggested [19] that impurities assemble to form highly compensated micro-inhomogeneities. That hypothesis seems to be confirmed by the microprecipitates we find in CTZ V 13 from thermal conductivity data.

5.2 TELLURIUM AND CADMIUM PRECIPITATION. — In all cases the volume of the precipitates is greater

than the foreign atoms content. Therefore precipitation of excess Tellurium can be considered because of the higher volatility of Cadmium. Electrical measurements indicate that the solidus in CdTe diagram is retrograde. For example, in samples pulled by THM at 700°C , a decrease of five orders of magnitude of the Tellurium solubility occurs during the cooling to room temperature [20].

The existence of these microprecipitation processes is now confirmed by Magee *and al.* [22] with Transmission Electron Microscopy observations. It has been shown that many of the macroscopic defects observed in infrared microscopy are composed of aggregation of :

- Tellurium precipitates.
- In_2Te_3 or CdCl_2 platelets in the case of Indium or chlorine doped samples.
- Dislocations.
- Stacking-faults.

5.3 THERMAL TREATMENT. — Magee *and al.* [22] have shown that annealing at temperatures over 500°C decomposes only Tellurium precipitates. In order to determine the precipitation mechanism, we have annealed at 580°C during 18 h, in a silica tube sealed under 10^{-5} torr, a specimen refined by vertical zone melting technique. Thermal conductivity data (Fig. 6) after annealing show a great increase in

FIG. 6. — Thermal conductivity before and after annealing of a sample refined by vertical zone melting technique.

point defect concentration from $9.4 \times 10^{17} \text{ cm}^{-3}$ to $2.8 \times 10^{18} \text{ cm}^{-3}$, and a decrease in precipitates diameter from $108 \text{ \AA}$ to $82 \text{ \AA}$ (best fit values). If we suppose that Tellurium moves through the lattice in Tellurium position, we can evaluate the number of atoms which disperse in the lattice when the precipitate volume decreases. This dispersion of Tellurium corresponds to an increase in point defect concentration since an excess of Tellurium can be interpreted as Cadmium vacancies. The decrease of the precipitate volume is :

$$V_p = C(D_1^2 - D_2^2) \frac{\pi}{6}$$

$$= 5.6 \times 10^{19} \text{ \AA}^3 \text{ cm}^{-3}$$

where C is the precipitate concentration, D_1 and D_2 are the initial and final diameters of the precipitates. With an average volume of $34 \text{ \AA}^3$ per atom [2] V_p can be associated to an increase of $1.6 \times 10^{18} \text{ cm}^{-3}$ in point defect concentration which varies from $9.4 \times 10^{17} \text{ cm}^{-3}$ to $2.6 \times 10^{18} \text{ cm}^{-3}$ if all Tellurium atoms stay on lattice sites.

The Callaway model applied to our thermal conductivity measurement leads to a value of $2.8 \times 10^{18} \text{ cm}^{-3}$ which is in very good agreement with the preceeding evaluation. This implies low contamination by impurity diffusion from the quartz during annealing.

6. Conclusions. — This investigation which agrees with Magee *and al.* [22] shows the presence in all specimens of microprecipitates of about $100 \text{ \AA}$ of

diameter. However X-ray topography shows that some precipitates can aggregate into macroscopic defects ($\geq 1 \mu\text{m}$). The different elaboration methods seem to have reached a limiting value of purity depending of a contamination-purification equilibrium [19]. The research for increasing the quality of CdTe requires additional investigations to determine the behaviour of microdefects after thermal annealing shedules [22].

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References

- [1] HOLLAND, M. G., *Phys. Rev.* **134** (1964).
- [2] SLACK, G. A., GALGINAITIS, S., *Phys. Rev.* **133** (1964).
- [3] SLACK, G. A., *Phys. Rev.* **6** (1972) 10.
- [4] VUILLERMOZ, P. L., PINARD, P., DAVOINE, F., *Revue Phys. Appl.* **3** (1968) 11.
- [5] VUILLERMOZ, P. L., PINARD, P., *C. R. Hebd. Seán. Acad. Sci. Paris* **269** (1969) 1193.
- [6] VUILLERMOZ, P. L., Thèse, Lyon (1973).
- [7] CALLAWAY, J., *Phys. Rev.* **113** (1959) 1046.
- [8] NETTLETON, R. E., *Phys. Rev.* **132** (1963) 2032.
- [9] BERMAN, R., BROCK, J. C. F., *Proc. R. Soc. A* **289** (1965).
- [10] KLEMENS, P. G., *Proc. Phys. Soc.* **68** (1955) 1113.
- [11] KYLE, N. R., *Proc. Intern. Symp. on CdTe* (P. Siffert, A. Cornet Editors, Strasbourg) 1971.
- [12] ZANIO, K., *Proc. Intern. Symp. on CdTe* (P. Siffert, A. Cornet Editors, Strasbourg) 1971.
- [13] BELL, P. O., WALD, F., *Proc. Intern. Symp. on CdTe* (P. Siffert, A. Cornet Editors, Strasbourg) 1971.
- [14] SMITH, C. S., GUTTMAN, L., *Trans. AIME* **197** (1953) 81.
- [15] FVRUSHO, K., *Japan, J. Appl. Phys.* **5** (1964).
- [16] CHIKAWA, J., *Appl. Phys. Lett.* **4** (1964) 25.
- [17] LANG, A. R., SHAH, C. J., *Mineral Magazine* **33** (1963) 594.
- [18] KISELEVA, K. V., KLEVKOV, U. V., MAXIMOVSKY, S. N., MEDVEDEV, S. A., SENTURINA, N. N., *Proc. Intern. Symp. on CdTe* (P. Siffert, A. Cornet Editors, Strasbourg) 1971.
- [19] TRIBOULET, R., MARFAING, Y., *Jour. Electrochem. Soc.* **120** (1973) 9.
- [20] CORNET, A., Thèse, Strasbourg (1976).
- [21] SCHAUB, B., POTARD, L., *Proc. Intern. Symp. on CdTe* (P. Siffert, A. Cornet Editors, Strasbourg) 1971.
- [22] MAGEE, T. J., PENG, J., BEAN, J., *Phys. Stat. Sol. (a)* **27** (1975) 557.