Influence of the stoichiometry deviation on the electrical properties of MoTe2-x

A. Bonnet, A. Conan, M. Spiesser, M. Zoaeter

To cite this version:
A. Bonnet, A. Conan, M. Spiesser, M. Zoaeter. Influence of the stoichiometry deviation on the electrical properties of MoTe2-x. Journal de Physique, 1988, 49 (5), pp.803-811. <10.1051/jphys:01988004905080300>. <jpa-00210757>

HAL Id: jpa-00210757
https://hal.archives-ouvertes.fr/jpa-00210757
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Influence of the stoichiometry deviation on the electrical properties of MoTe$_{2-x}$

A. Bonnet (1), A. Conan (1), M. Spiesser (2) and M. Zoaeter (3)

(1) Laboratoire de Physique Cristalline, U.A. CNRS n° 802, Université de Nantes, 2 rue de la Houssinière, 44072 Nantes Cedex 03, France
(2) Laboratoire de Chimie des Solides, L.A. CNRS n° 279, Université de Nantes, 2 rue de la Houssinière, 44072 Nantes Cedex 03, France
(3) Université Libanaise, Faculté des Sciences (Section I), Beyrouth, Liban

(Reçu le 21 mai 1987, révisé le 4 novembre 1987, accepté le 27 janvier 1988)

Résumé. — Les mesures des coefficients de transport (conductivité électrique, effet Hall, pouvoir thermoélectrique) ont été effectuées sur des monocristaux de MoTe$_{2-x}$ ($x = 0.01$ et $0.015$) dans une gamme étendue de température. Les échantillons ont été préparés par une méthode à base de flux de tellure et l'écart à la stoechiométrie a été obtenu par un traitement thermique. Les écarts expérimentaux sont interprétés sur la base d'un modèle de semi-conducteur de type p compensé. L'origine lacunaire des deux niveaux d'impuretés est clairement mise en évidence. Pour un écart faible à la stœchiométrie, les porteurs de charge sont diffusés de deux façons différentes : impuretés ionisées et modes de réseau thermiques. Pour un plus grand écart, les niveaux donneurs et accepteurs s'élargissent en deux bandes étroites d'énergie. A basse température, les mécanismes de conduction sont principalement gouvernés par des sauts activés thermiquement de petits polarons dans ces bandes. A plus haute température, la contribution des états étendus doit être prise en compte. Il est également montré que la présence de sites lacunaires de tellure conduit à une plus grande polarisation du matériau et à une interaction beaucoup plus importante entre la bande de valence et la bande d'accepteurs. Le modèle adopté ici est de manière générale en accord avec la structure de bande des dichalcogénures des métaux de transition du groupe VI à coordination trigonale prismatique.

Abstract. — Transport coefficient measurements (electrical conductivity, Hall effect, thermoelectric power) have been performed on single crystals of MoTe$_{2-x}$ ($x = 0.01$ and $0.015$) in a wide range of temperatures. The samples were prepared by a based Te flux method and the deviation from stoichiometry was obtained by a thermal treatment. Experimental results are interpreted on the basis of a compensated p-type semiconductor model. The lacunar origin of the two impurity levels is clearly shown. For a weak departure from stoichiometry, the carriers are scattered in two ways : ionized impurities and thermal lattice modes. For a larger departure, the donor and acceptor levels broaden in two narrow energy bands. At low temperatures, the conduction mechanisms are mainly governed by a thermal hopping of small polarons in these bands. At higher temperatures, the contribution of the extended states must be taken into account. It is shown that the presence of Te-lacunar-sites leads to a greater polarization of the material and a much higher interaction between the valence and the acceptor energy bands. The model adopted here is in agreement with the band structure of the group VI transition metal dichalcogenides which have a trigonal prism coordination.

1. Introduction.

Lamellar dichalcogenides of transition elements TX$_2$ have been recently the subject of an increasing interest since it has been shown that they can be used successfully in intercalation chemistry [1-4]. The electrical properties of the subsequent compounds obviously depend upon the intercalated species, but also upon the band structure of the host matrix and the energy values involved in the electronic transfers. A possible approach is to study the behaviour of the transport phenomena (electrical conductivity, thermoelectric power, Hall effect) of the host compound in a wide temperature range. Then, details on the band structure of the material near the Fermi level
can be easily deduced from this study. In way, measurements of the electrical conductivity $\sigma$ and thermoelectrical power $S$ have been recently performed [5] on MoTe$_2$ crystals prepared by a vapor phase transport method. Bromine was used as the transport agent and the very important role played by the energy levels associated with this impurity was clearly evidenced (MoTe$_2$-$n$ type). Even more recently [6], similar experiments were carried out between 77 and 700 K on MoTe$_2$ crystals prepared by a based Te flux method [7].

These new compounds, quasi-intrinsic, have allowed us to specify the band structure model and to determine the role of the d orbitals in the establishment of covalent bondings $A$ very weak deviation from stoichiometry due to the preparation leads to a weak $p$ character for these compounds. Experimental results were interpreted in terms of a classical model for a semiconductor having an acceptor level $E_A$ located 130 meV above the valence band. This model agrees well with the band structure model for dichalcogenides of groupe VI metal transition compounds [8-12]. We have assumed that the lack of some Te atoms leads to the existence of localized d levels in the gap, due to Mo neighbours whose covalent bondings are no longer satisfied. Then, it seemed to us interesting to check this hypothesis by increasing the role played by the d electrons in performing a controlled decrease of the Te content. In order to do so, the electrical conductivity and the thermoelectric power of MoTe$_{2-x}$ crystals ($x = 0.01, 0.015$) were measured within a large range of temperatures (77-700 K). The band structure model of these non-stoichiometric compounds is a continuation of that obtained for MoTe$_2$. In addition, an extra compensating level $E_D$ located above the acceptor level ($E_D - E_V \approx 200$ meV) is found.

The semiconductor is compensated and the random potential due to charged acceptors and donors induces a broadening of the corresponding levels $E_A$ and $E_D$ into narrow bands. As a consequence, in MoTe$_{1.985}$, these bands participate to the conduction in the form of thermally activated hopping of small polarons.

2. Experimental results.

Non-stoichiometric crystals have been obtained by decreasing in a controlled way the Te content in MoTe$_2$ compounds. The stoichiometric MoTe$_2$ crystal is precisely weighed and then introduced in a quartz tube whose diameter is 8 mm and length 300 mm. The tube is sealed under vacuum. The side of the tube where the crystal has been put is heated up to 660 °C whereas the other side is kept outside the furnace. Te is sublimated and condensates on cold walls. The decrease of the Te content is proportional to the heating time varying from one to two days according to the desired composition. Finally, the crystal is annealed at 550 °C during two or three days in another quartz tube in order to make the vacancy distribution homogeneous because of the treatment which is initially efficient mainly at the surface of the sample.

The composition of the compound is determined from weight measurements before and after taking off the Te which is also weighed. The determination of the composition value $2 - x$ is in average within an accuracy of about 1 %. X-rays diffraction patterns performed in a Guinier chamber, are practically unperturbed by the Te decrease.

The electrical conductivity $\sigma$ and the thermoelectric power $S$ of crystals, with a composition MoTe$_{1.991}$ and MoTe$_{1.985}$ respectively, have been measured between 77 and 700 K in the hexagonal planes. Several experimental measurements have been taken on each sample. A good reproducibility was obtained and experimental data were always

![Fig. 1a. — Experimental variations of ln $\sigma$ versus $10^3/T$ obtained for MoTe$_{1.991}$. The theoretical variation is drawn as a full line.](image1)

![Fig. 1b. — Experimental variations of T.E.P. versus $10^3/T$ obtained for MoTe$_{1.991}$. The theoretical variation is drawn as a full line.](image2)
within the error bars determined for each technique, i.e. \( \sim 2\% \) for conductivity and \( \sim 5\% \) for T.E.P.

Two characteristic behaviors have been experimentally observed:

- \( \text{MoTe}_{1.991} \): \( \ln \sigma \ (\Omega^{-1} \text{cm}^{-1}) \) and \( S \ (\mu \text{V/K}) \) \( 10^3/T \) are plotted in figures 1a and b. The electrical conductivity is found to be of the order of \( 9 \times 10^{-4} \ (\Omega \text{cm})^{-1} \) at liquid nitrogen temperature. It increases until \( 0.28 \ (\Omega \text{cm})^{-1} \) at \( 310 \ K \) and then decreases to \( 0.24 \ (\Omega \text{cm})^{-1} \) around \( 500 \ K \).

For higher temperatures, the intrinsic regime is reached and \( \sigma \) increases rapidly until \( 2.5 \ (\Omega \text{cm})^{-1} \) around \( 700 \ K \). In this temperature range, a thermal activation energy can be evaluated to \( 0.4 \) eV.

Between \( 77 \ K \) and room temperature, the T.E.P. decreases slowly and quasi-linearly from \( 100 \) to \( 700 \ \mu \text{V/K} \) (ionization domain) with a thermal activation energy nearly equal to \( 65 \) meV. Between \( 300 \) and \( 500 \ K \), \( S \) is approximatively constant (exhaustion domain) and then drops rapidly versus temperature in the intrinsic domain;

- \( \text{MoTe}_{1.985} \): \( \ln \sigma \) and \( S \) versus \( 10^3/T \) are represented in figures 2a and b. The electrical conductivity has a behavior similar to that observed in \( \text{MoTe}_2 \) and \( \text{MoTe}_{1.991} \). Nevertheless, experimental data exhibit a more pronounced discrepancy with respect to the linear law and the values of \( \sigma \) are found much higher (\( 0.8 \ (\Omega \text{cm})^{-1} \) at room temperature).

The T.E.P. coefficient has a very characteristic behavior, different from that observed in previous compounds. At low temperatures, \( S \) slightly increases from \( 50 \) to \( 220 \ \mu \text{V/K} \) from \( 77 \) to \( 180 \ K \). Then, it has relatively small variation until \( 330 \ K \) since the maximum value measured at \( 240 \ K \) is found \( 230 \ \mu \text{V/K} \). At higher temperatures, \( S \) drops down drastically (\( 50 \ \mu \text{V/K} \) at \( 650 \ K \)) and behaves similarly to what is observed in \( \text{MoTe}_2 \) and \( \text{MoTe}_{1.991} \).

Fig. 2a. — Experimental variations of \( \ln \sigma \) versus \( 10^3/T \) obtained for \( \text{MoTe}_{1.985} \). The theoretical variation is drawn as a full line.

Fig. 2b. — Experimental variations of T.E.P. versus \( 10^3/T \) obtained for \( \text{MoTe}_{1.985} \). The theoretical variation is drawn as a full line.

Properties of \( \text{MoTe}_{1.991} \) are very similar to those of stoichiometric compounds. Although T.E.P. is slightly smaller, experimental curves of \( \ln \sigma \) and \( S \) are very similar. On the contrary, \( \text{MoTe}_{1.985} \) has a behavior much less characteristic of a semiconductor; for example, the variations of \( S \) cannot be interpreted in the frame of the model elaborated for the stoichiometric compound. This result is close to what is observed in \( \text{MoTe}_{2-x} \) in powder form [13].

Fig. 3. — Schematic OK band model here adopted for the two non-stoichiometric compounds.

3. Theoretical results.

The experimental curves reported here for \( \text{MoTe}_{2-x} \) crystals cannot be well fitted using the model developed for stoichiometric compounds. Therefore, a modified model, derived from the previous one, is proposed here. It consists in the introduction of an additional donor level \( E_D \), located just above the acceptor level \( E_A \) (Fig. 3). Since such an approach is absolutely necessary to interpret transport properties in \( \text{MoTe}_{1.985} \), we also used it for \( \text{MoTe}_{1.991} \).
3.1 MoTe$_{1.991}$ ANALYSIS. — At low and medium range temperatures, the main contribution to the electrical conductivity and to the T.E.P. comes from excited holes in the valence band where they are expected to interact with both ionized impurities and long wavelength acoustic phonons. At higher temperatures, the contribution of excited electrons in the conduction band has to be taken into account where they interact with acoustic vibration modes. $E_A$ and $E_D$ are still considered as narrow levels and therefore the electrons which occupy these levels are localized.

In the overall range of temperatures investigated, electrical conductivity and thermoelectric power can be expressed as follow:

$$\sigma = \sigma_n + \sigma_p = \sigma_n + \sigma_{t,i} = \sigma_n + \frac{1}{\rho_t + \rho_i} \quad (1)$$

in which:

$$\sigma_n = ne\mu_i \left( \frac{T}{T_0} \right)^\alpha$$

and:

$$\sigma_p = pe\mu_i \left( \frac{T}{T_0} \right)^\alpha, \quad \sigma_{t,i} = pe\mu_i \frac{N_i}{N_1} \left( \frac{T}{T_0} \right)^\delta$$

where $n$, $p$, $N_1$ are the concentrations in electrons, holes and ionized impurities ($N_A + N_D$) respectively. The $t$ and $i$ indices are related to the collision mechanisms with the lattice and with the ionized impurities respectively whereas the 0 index denotes room temperature:

$$S = \frac{\sigma_n S_n + \sigma_{t,i} S_{t,i}}{\sigma} \quad \text{with} \quad S_{t,i} = \frac{\rho_t S_t + \rho_i S_i}{\rho_t + \rho_i}$$

and:

$$S_n = \frac{k}{e} \left\{ \beta (E_C - E_F) + A \right\}$$

$$S_t = \frac{k}{e} \left\{ \beta (E_F - E_V) + A \right\}$$

$$S_i = \frac{k}{e} \left\{ \beta (E_F - E_V) + D \right\} \quad (2)$$

- $\beta$ designs $1/kT$.
- $A$ and $D$ are kinetic coefficients associated with collision mechanisms.

In this two-level model, the electrical neutrality is written:

$$n + N_A = p + N_D^+$$

The concentration of carriers and ionized impurities can be expressed using the quantity:

$$X = \exp[-\beta (E_F - E_V)]$$

and therefore:

$$n = N_{C0} \left( \frac{T}{T_0} \right)^{1.5} \frac{\exp(-\beta \Delta)}{X} \quad (3)$$

$$p = N_{V0} \left( \frac{T}{T_0} \right)^{1.5} X \quad (4)$$

$$N_A^- = \frac{N_A}{1 + 2X \exp[\beta (E_A - E_V)]} \quad (5)$$

$$N_D^+ = \frac{N_D}{1 + 2X \exp[-\beta (E_D - E_V)]} \quad (6)$$

$N_{C0}$ and $N_{V0}$ are equivalent densities of states in the conduction and valence bands respectively, calculated at room temperature $T_0$. $\Delta$ is the gap and we have assumed that its value has a linear dependence versus temperature, similarly to what is observed in MoTe$_2$ [14]:

$$\Delta = (E_C - E_V)_{0K} - \gamma T \quad (\gamma = 5 \times 10^{-4} \text{ eV.K}^{-1}) \quad (7)$$

In the expressions giving $N_A^-$ and $N_D^+$, the factor 2 is a spin factor which takes into account the probabilities of the electron trapping and emission at the impurity level.

Measurements of the Hall constant at room temperature ($R_H = 240 \text{ cm}^2/\text{C}$) allows a calibration of the concentrations.

Theoretical curves of $\ln \sigma$ and $S$ in MoTe$_{1.991}$ are represented in solid lines in figures 1a and b. At very low temperatures, a small displacement from the linear law appears in figure 1a; it can be eventually interpreted by an additional contribution, still weak, of a hopping conduction in the $E_A$ level expected very slightly broadened. The variation of the Fermi level location as a function of temperature (Fig. 4) lets us suppose that this extra conduction could occur at the Fermi level.

![Fig. 4. — Theoretical variations of the Fermi level position versus $T$. The zero energy is arbitrary chosen on $E_V$. (1) MoTe$_{1.991}$, (2) MoTe$_{1.965}$, (1') and (2') are the respective ionization energies of the acceptor levels.](image-url)
The different contributions to the electrical conductivity and T.E.P. are shown in figures 5a and b. In particular, in figure 5b, the main interaction holes-ionized impurities at low temperatures, replaced by a holes-acoustical phonons interaction at high temperatures is evidenced. The values of the physical parameters which give the best fit to the experimental curves are listed in table I.

![Fig. 5a. — Electrical resistivity contributions of MoTe$_{1.991}$, (1) $\rho$, (2) $\rho_{\perp}$, (3) $\rho_{1}$, (4) $\rho_{n}$.](image)

![Fig. 5b. — T.E.P. contributions of MoTe$_{1.991}$, (1) $S$, (2) $\sigma_{1/1}/\sigma$, (3) $\sigma_{n}/\sigma$.](image)

### Table I. — The values of physical constants which are reported refer to the conduction in the extended states.

<table>
<thead>
<tr>
<th></th>
<th>MoTe$_{1.991}$</th>
<th>MoTe$_{1.985}$</th>
<th>MoTe$_2$ (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$ (eV)</td>
<td>$0.95 - 5.4 \times 10^{-4} T$</td>
<td>$0.83 - 5.4 \times 10^{-4} T$</td>
<td>$0.98 - 5.4 \times 10^{-4} T$</td>
</tr>
<tr>
<td>$N_{e0}$ (cm$^{-3}$)</td>
<td>$1.0 \times 10^{19}$</td>
<td>$0.4 \times 10^{19}$</td>
<td>$1.1 \times 10^{19}$</td>
</tr>
<tr>
<td>$N_{d0}$ (cm$^{-3}$)</td>
<td>$3 \times 10^{18}$</td>
<td>$3 \times 10^{18}$</td>
<td>$3 \times 10^{18}$</td>
</tr>
<tr>
<td>$E_A - E_N$ (eV)</td>
<td>$0.060$</td>
<td>$0.028$</td>
<td>$0.130$</td>
</tr>
<tr>
<td>$N_A$ (cm$^{-3}$)</td>
<td>$4.8 \times 10^{16}$</td>
<td>$1.0 \times 10^{18}$</td>
<td>$3.2 \times 10^{16}$</td>
</tr>
<tr>
<td>$E_D - E_N$ (eV)</td>
<td>$0.21$</td>
<td>$0.21$</td>
<td>$0.21$</td>
</tr>
<tr>
<td>$N_D$ (cm$^{-3}$)</td>
<td>$2.5 \times 10^{16}$</td>
<td>$5.6 \times 10^{17}$</td>
<td></td>
</tr>
<tr>
<td>$\mu_i^f$ (cm$^2$/V.s)</td>
<td>$214 \left( \frac{N_{b0}}{N_1} \right) \left( \frac{T}{T_0} \right)^{1.6}$</td>
<td>$57 \left( \frac{N_{b0}}{N_1} \right) \left( \frac{T}{T_0} \right)^{1.5}$</td>
<td>$160 \left( \frac{N_{b0}}{N_1} \right) \left( \frac{T}{T_0} \right)^{2.2}$</td>
</tr>
<tr>
<td>$D(k/e)$</td>
<td>$4$</td>
<td>$3.8$</td>
<td>$4.7$</td>
</tr>
<tr>
<td>$\mu^f$ (cm$^2$/V.s)</td>
<td>$93 \left( \frac{T}{T_0} \right)^{-2.5}$</td>
<td>$12 \left( \frac{T}{T_0} \right)^{-2.7}$</td>
<td>$96 \left( \frac{T}{T_0} \right)^{-1.4}$</td>
</tr>
<tr>
<td>$A(k/e)$</td>
<td>$2$</td>
<td>$1.7$</td>
<td>$2.7$</td>
</tr>
<tr>
<td>$\mu_i^f$ (cm$^2$/V.s)</td>
<td>$426 \left( \frac{T}{T_0} \right)^{-1.5}$</td>
<td>$426 \left( \frac{T}{T_0} \right)^{-1.5}$</td>
<td>$426 \left( \frac{T}{T_0} \right)^{-1.5}$</td>
</tr>
<tr>
<td>$D(k/e)$</td>
<td>$-2$</td>
<td>$-2$</td>
<td>$-2$</td>
</tr>
</tbody>
</table>

(*) The values obtained on MoTe$_2$ (6) are given in order to make a comparison possible.
temperature range. We have supposed that the stoichiometry deviation leads to a broadening of $E_A$ and $E_D$ levels into narrow bands in which thermally activated hopping conduction mechanisms take place: vacancy centers induce a large polarization of the medium leading to the formation of small polarons.

Hopping conduction can be written in the general form [15]:

$$\sigma_H = \sigma_0 \exp[-2 \alpha R - \beta W]$$

in which $\alpha$ is the damping factor of the wave function, $R$ is the hopping distance between nearest neighbours and $W$ the hopping energy. The polaron term $W_H$ and the disorder $W_d$ [15] are included in $W$

$$W = W_H(T) + W_d/2$$

$W_H(T)$ follows the law:

$$W_H(T) = W_H \frac{\hbar x}{x}$$

where $\hbar \omega_0$ is an optical vibration quantum.

The conductivity $\sigma_H$ due to hopping between nearest neighbours sites is given, in the non-adiabatic regime, by:

$$\sigma_H = \frac{e^2}{4 \hbar R} \beta \epsilon (1 - c) \left[ \frac{\pi \beta}{4 W_H} \right]^{1/2} \Gamma^2 \exp(-\beta W)$$

where $I = I_0 \exp(-\alpha R)$ is the transfer integral between sites separated by $R$ with:

$$I_0 = \frac{3 e^2 \alpha}{2 \epsilon} \left[ 1 + \alpha R + \frac{(\alpha R)^2}{6} \right]$$

$c$ is the relative quantity of particles for which hopping can occur:

$$c = (N_D - N_D^0)/N_D \ or \ N_A^0/N_A$$

and $\epsilon$ is the static dielectric constant of the medium.

The expression of the associated T.E.P. is [16]:

$$S = \frac{k}{e} \ln \left( \frac{c}{1 - c} \right)$$

Other contributions to transport mechanisms such as holes in the valence band or electrons in the conduction band have been described above (§ 3.1).

On the whole temperature range investigated, the electrical conductivity is therefore the summation of the following terms:

$$\sigma = \sigma_n + \sigma_{\ell,i} + \sigma_H^A + \sigma_H^D$$

and $S$:

$$S = (\sigma_n S_n + \sigma_{\ell,i} S_{\ell,i} + \sigma_H^A S_{H}^A + \sigma_H^D S_{H}^D)/\sigma$$

(A and D superscripts refer to acceptor and donor levels respectively).

The Hall mobility due to hopping is generally much smaller than that observed in delocalized states in valence or conduction bands [17]. $R_H$ can therefore be calculated in the following approximation:

$$R_H \sim (-\sigma_n \mu_H^A + \sigma_p \mu_H^D)/\sigma^2.$$  

This expression is usable close to room temperature and therefore valid at higher temperatures. As shown in figures 2a and b, a good agreement is obtained between experimental data and theoretical results for both conductivity and T.E.P.

The contribution of electrons and holes to conductivity and T.E.P. are represented in figures 6a and 6b. Comparison can be made and it is shown in particular that, in the broadened acceptor level, the hopping conduction, which is the main contribution at low temperatures, becomes similar to that of holes ($\sigma_{\ell,i}$) around 150 K. On the contrary, the main contribution to the T.E.P. comes from holes in the valence band in the whole temperature range investi-
gated, whereas that of the donor level — very weak for the conductivity — becomes significant on T.E.P. at 300 K.

The Hall coefficient is 10.5 cm³/C at 300 K. We have checked it by using a Hall mobility for polarons similar to their conduction mobility, the polaronic contribution to \( R_H \) is still negligible. This is a good test for the approximation made for \( R_H \), allowing a calibration of the concentrations. Therefore, in the valence band, the equivalent density of states \( N_{v0} \) is \( 4 \times 10^{18} \text{ cm}^{-3} \) at 300 K.

The values of the physical parameters which give the best fit to the experimental curves are listed in table I and table II.

### Table II. — The values of physical constants obtained for the hopping conduction in the narrow bands \( E_A \) and \( E_D \) of MoTe₁.₉₈₅.

<table>
<thead>
<tr>
<th>( W_A ) ( \text{meV} )</th>
<th>( W_D ) ( \text{meV} )</th>
<th>( \mu_A ) ( \text{meV} )</th>
<th>( W_A ) ( \text{meV} )</th>
<th>( \mu_D ) ( \text{meV} ) cm²/V.s</th>
<th>( \mu_D ) ( \text{meV} ) cm²/V.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.5</td>
<td>39.5</td>
<td>41</td>
<td>7.5</td>
<td>7.5</td>
<td>3.4</td>
</tr>
</tbody>
</table>

### 4. Discussion.

First of all, it appears that the concentration of the acceptor and donor sites respectively both increases as the Te content decreases in the compound, whereas the \( N_D/N_A \) compensation is close to 0.5. Obviously, the origin of the donor and acceptor levels is lacunary. The semiconductor is weakly compensated and the random potential of acceptor and donor charged centers induces a broadening of the corresponding \( E_A \) and \( E_D \) levels into narrow bands. Then in MoTe₁.₉₈₅, they participate in the conduction by thermally activated hoppings of small polarons.

Another point is that the acceptor broadened level goes closer to the valence band as the stoichiometry deviation increases. Thus, \( E_A - E_V \) is found to be about 130 meV for MoTe₂ [6] and decreases until 28 meV for MoTe₁.₉₈₅. This energy difference, \( E_A - E_V \), which can be interpreted as the formation energy of a negative ion from a neutral atom is given by:

\[
E_A - E_V = \frac{m^* Z^2 e^4}{\hbar^2 e^2} \epsilon_0 \epsilon_r
\]

in which \( m^* \) is the effective mass in the valence band and the effect of the crystal potential is neglected.

We have calculated an approximate value for the macroscopic static dielectric constant for the compound whose composition is close to stoichiometry \( (E_A - E_V = 130 \text{ meV}) \). For the second and the third acceptor states of charge, calculated values are either compared to those found in the literature [18] or measured in the laboratory by the capacitive method at room temperature \( (\epsilon = 16) \). A good agreement is found if the lacunary centres are assumed to be in the second acceptor state of charge.

For two crystals having a different composition, the effective mass \( m^* \) ratio is equal to the effective mass ratio of the density of states. The effective mass which has been found for MoTe₁.₉₉₁ being very little dependent upon the deviation from stoichiometry \( (m^* = 0.55 m_e \text{ for MoTe}_2 \text{ to be compared to } m^* = 0.52 m_e \text{ for MoTe}_1.₉₉₅ \text{ — Tab. 1}) \), the \( E_A - E_V \) decrease is partially characteristic of an increase of the dielectric constant and is an additional proof that the larger the stoichiometry deviation, the more polarized the material.

In MoTe₂₋ₓ compounds, because the donor level is located above the acceptor level, the hypothesis of multivalent lacunary centres must be rejected. The concentration of the \( E_A \) level is significantly smaller than the total vacancy concentration which is deduced from the composition value. Therefore, we think that these levels come rather from vacancy-vacancy associations.

Although the origin of the donor level is probably associated with the Te content decrease, its exact nature must be investigated in relation with the structure modifications in valence bondings. A certain amount of d electrons from molybdenum atoms are no longer participating in d-p bondings of the valence band. This structural disorder is probably small and does not significantly modify powder X-ray diffraction patterns obtained on non-stoichiometric compounds. To explain this, it must be assumed that these electrons are only very weakly interacting with the semiconductor atoms and that their orbital radius is small. Indeed, d electrons localized on some Mo atoms must behave similarly. The \( E_D \) level, as it has been located, must be considered as a deep level.

The small polaron model proposed for the MoTe₁.₉₈₅ compound is applied in expecting the non-adiabatic transfer of the self-trapped electrons. The transfer integral \( I \) is numerically calculated from the hopping conduction expression given in paragraph 3.2. The integral has to satisfy some criteria which affect the validity of the model:

- (a) it must remain small \( (I < 0.1 \text{ eV}) \);
- (b) the polaron radius \( r_p \) calculated from the expression \( r_p = R \frac{I}{W_H} \) (19) must remain smaller than the inter-site distance \( R \), for which an estimate is given if we suppose a spherical symmetry for the volume occupied by an impurity;
- (c) the tendency of the electron to become delocalized after having left its trap must be small: \( I^2/W_H kT \ll 1 \).
Table III. — Physical constants obtained for the small polaron model proposed for the MoTe$_1.985$ compound.

<table>
<thead>
<tr>
<th></th>
<th>$E_A$ narrow band</th>
<th>$E_D$ narrow band</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ (Å)</td>
<td>$l$ (meV)</td>
<td>$l/W_0$</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The results obtained are tabulated in table III and it appears that the above criteria are verified as well as the non-adiabatic one:

$$I^2/(h\omega_0 \sqrt{W_0/kT_0}) < 1.$$  \hspace{1cm} (17)

The polaron radius ($\approx 10$ Å) is much smaller than the distance between impurity sites and leads to a reasonable value for the relative dielectric constant for the polaron. The deduced ratio $\varepsilon/\varepsilon_0$ is comparable to that observed in many ionic crystals [20]. The macroscopic static dielectric constant being assumed to be approximately equal to 40, the localization length $\alpha^{-1}$ is found to be nearly equal to 20 Å. This value is consistent with the hypothesis of the electron tunnelling from one site to a neighboring site during a thermally activated hopping process.

The coupling constant $\gamma (= W_p/h\omega)$ is found to be of the order of 2, in agreement with what is generally taken ($2 < \gamma < 7$) [21].

The band width $B$ for small polarons can be expressed in terms of the transfer integral, the coupling constant, and the coordination number $z$:

$$B = 2zI \exp(-\gamma)$$ \hspace{1cm} (18)

if $z = 6$, we find $B = 8$ meV.

With this value, the thermoelectric power follows the classical Heikes' law (which assumes the band width to be smaller than $k_B T$) in the whole investigated domain.

5. Conclusion.

In this paper, we have clearly evidenced the role played by lacunary centres in MoTe$_{2-x}$ compounds.

- For a small stoichiometry deviation $x$, a deep donor level compensates the semiconductor.
- For a larger value of $x$ (MoTe$_{1.985}$), acceptor and donor levels broaden into narrow bands in which conduction mechanisms of hoppings of small polarons take place. At the same time, the decrease (by a factor of more than 2) of the equivalent density of states of the valence band is associated with weak deformations of the crystalline structure which may affect the extension and eventually the nature of the orbitals. In other words, the modification of the curvature of the valence band must be attributed to the interaction between the valence band and the narrow band $E_A$ which is very close to $E_V$ ($E_A - E_V = 28$ meV).

The electrons participate only at high temperatures. This is an essential point in discussing the parameters involved in the conduction band. All of them cannot be determined since the electrical conductivity is thermally activated in the explored temperature domain. The equivalent density of states in the conduction band has been assumed to be constant and equal to that determined for an n-type MoTe$_2$ single crystal [4]. As a matter of fact, the conduction band shape is very little dependent on the $E_A$ and $E_D$ levels which are located far away from it.

We have chosen the gap width as an adjustable parameter whereas its variation coefficient with temperature has been kept constant (0.54 meV/K). The decrease of the gap width for a stoichiometry deviation increase clearly indicates a softening of valence bondings. On the other hand, the lattice mobility variations calculated at 300 K as a function of the stoichiometry deviation are very characteristic. For compounds in which a conduction by hopping between localized states in the narrow bands $E_A$ and $E_D$ does not take place, i.e. MoTe$_2$ and MoTe$_{1.99}$, the above variation is similar but it decreases rather significantly for MoTe$_{1.985}$. The phononic spectrum of the crystal is therefore affected by the Te content decrease. Nevertheless, these values reflect all scattering mechanisms in the valence band and must not be taken too quantitatively. The stoichiometry deviation favours the polarization of the material and so, optical modes cannot be neglected. Therefore, the mobility dependence expressed in $T^{-2.5}$ is then, in an approximate way, the total dependence if the mobility results from the two mechanisms (acoustical modes-optical modes).

Moreover, it must be noticed that other exponents in mobilities as well as kinetic terms in the thermoelectric power are practically similar to their theoretical values.

To conclude, we can recall that the adiabatic regime has been tested for the conduction mechanisms involving hoppings in MoTe$_{1.985}$ but the adiabaticity criterion is not verified. This is a reason for rejecting this regime. The good agreement between measured and calculated values, together with the simplicity of the model, allow us to expect a continuation of these studies in other compounds whose Te content is even smaller and for which the band structure model would be built in a continuous way from what is proposed here.
Acknowledgments.

We are indebted to Pr. S. Lefrant for helpful discussions.

References