JOURNAL OF MATERIALS SCIENCE 32 (1997) 2445–2449

Tellurium depletion electrical effects in $MoTe_{2-x}$ single crystals doped with bromine

M. MORSLI, A. BONNET, V. JOUSSEAUME, L. CATTIN, A. CONAN
Laboratoire de Physique des Matériaux pour l'Electronique, EA 1153, Faculté des Sciences et des Techniques, 2 rue de la Houssinière, 44072 Nantes Cédex 03, France

M. ZOAETER
Faculté des Sciences I Université Libanaise, Beirut, Lebanon

Electrical conductivity and thermoelectric power measurements have been performed on *n*-type $MoTe_2$-single crystals in a wide temperature range (125–770 K). Stoichiometric samples were prepared by vapour transport with bromine as transport reagent. The experimental results which have been performed along a direction perpendicular to the c-axis, are analysed with the model already used for *p*-type $MoTe_{2-x}$ single crystals grown in a molten tellurium bath without any contaminating reagent. A bromine donor level which is located near the bottom of the conduction band is found and takes into account all the new experimental results. The semiconductor is compensated and the random potential due to the charged lacunar sites and bromine impurities induces a broadening of this level into a narrow band for the compound with the larger tellurium depletion. This band contributes to the conduction in the form of thermally activated hopping. The schematic band structure deduced from transport measurements is in good agreement with the electronic band structure of the group VI transition metal dichalcogenides with trigonal prism coordination.

1. Introduction

Lamellar dichalcogenides of transition elements TX_2 have been recently the subject of increasing interest since it has been shown that they can be used successfully in intercalation chemistry [1–4]. The particular photoelectrochemical properties of transition metal dichalcogenides enable a large variety of new applications to be explored. One of the important advantages associated with these materials over other chalcogenides and III–V semiconductors is that for the former case the photogenerated holes belong to non-bonding d orbitals and hence cannot participate in corrosion reactions [5, 6].

Measurements of the electrical conductivity σ and thermoelectrical power S have been recently performed [7] on $MoTe_2$ crystals prepared by a vapour phase transport method. Bromine was used as the transport agent and the very important role played by the energy level associated with this impurity was clearly evidenced for *n*-type $MoTe_2$, i.e. a donor level was found to be located at 9.5 meV from the conduction band.

More recently [8, 9], similar experiments were carried out between 77 and 700 K on *p*-type $MoTe_{2-x}$ crystals prepared by a based Te flux method [10].

It seemed to us interesting to check the role played by bromine upon the transport mechanisms of non-stoichiometric *n*-type crystals and the subsequent effects on their band structure. In order to do so, the electrical conductivity and the thermoelectric power of $MoTe_{2-x}$ crystals ($x = 0.015, 0.03$) were measured within a wide range of temperature (120–700 K). The band structure model of these non-stoichiometric compounds is found to be a continuation of that obtained for *p*-type $MoTe_2$.

2. Experimental procedure and electrical measurements

The experimental technique which has been used for the electrical conductivity and thermoelectric power (TEP) is based upon an automatic data acquisition system [11]. The ohmicity has been tested by drawing the *I–V* characteristics. In order to have access to the electrical conductivity, the room-temperature conductivity is measured by the Van der Pauw method.

The measurements (accuracy 2% for σ and 5% for S) have been performed on the non-stoichiometric crystals with the composition $MoTe_{1.985}$ and $MoTe_{1.97}$. The composition of the compound is determined from weight measurements before and after subtracting the Te which is also weighed. The determination of the composition value $2 - x$ is on average within an accuracy of about 0.5%. X-ray diffraction patterns, performed in a Guinier chamber, are practically unperturbed by the Te decrease.

The experimental variations of $\log \sigma$ ($\Omega^{-1}\,cm^{-1}$) and S($\mu V\,K^{-1}$) versus $10^3/T$ (K^{-1}) are plotted for $MoTe_{1.985}$ and $MoTe_{1.97}$ in Figs 1a and b and 2a and b, respectively. The electrical conductivity is found to

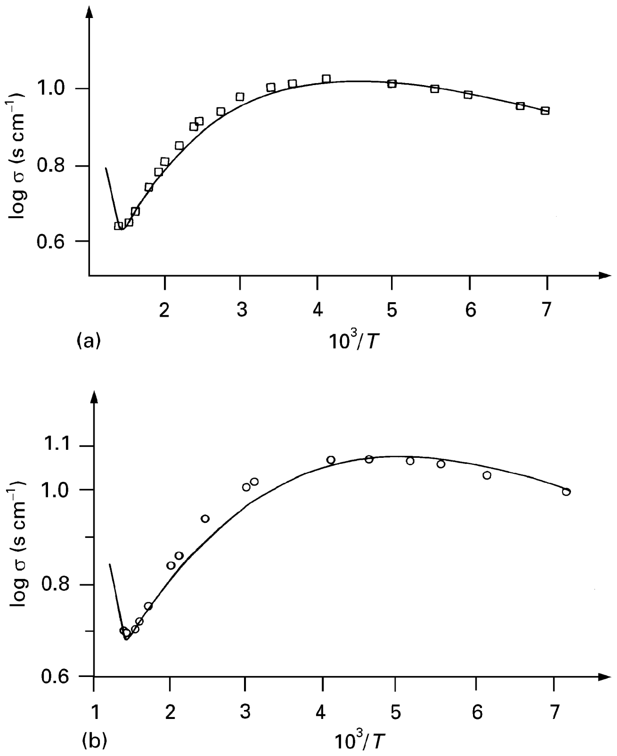

Figure 1 (a) Electrical conductivity variations $\log\sigma$ versus $10^3/T$ of $MoTe_{1.985}$. Dots are experimental data and the full line is the theoretical fit obtained with parameters listed in Table I. (b) Electrical conductivity variations $\log\sigma$ versus $10^3/T$ of $MoTe_{1.97}$. Dots are experimental data and the full line is the theoretical fit obtained with parameters listed in Table I.

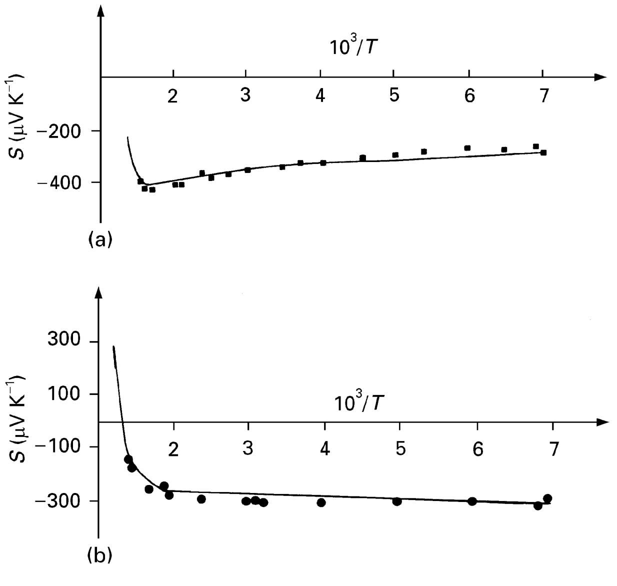

Figure 2 (a) Thermoelectric power variations S versus $10^3/T$ of $MoTe_{1.985}$. Dots are experimental data and the full line is the theoretical fit obtained with parameters listed in Table I. (b) Thermoelectric power variations S versus $10^3/T$ of $MoTe_{1.97}$. Dots are experimental data and the full line is the theoretical fit obtained with parameters listed in Table I.

be of the order of $2.5\,\Omega^{-1}\,cm^{-1}$ ($2.7\,\Omega^{-1}\,cm^{-1}$) at room temperature. It decreases slowly down to a minimum $1.9\,\Omega^{-1}\,cm^{-1}$ ($2\,\Omega^{-1}\,cm^{-1}$) which is reached at about 700 K.

The behaviour of the TEP coefficient S, which is negative over the whole temperature range investigated, is characterized by a relatively small variation. All these results can be significantly compared to those which have been obtained on the stoichiometric n-type $MoTe_2$ [7]. The following features as the departure from stoichiometry increases must be noticed: the electrical conductivity is an increasing function of x whereas the TEP, which shows a classical n-type behaviour for $MoTe_{1.985}$, correlatively decreases with tellurium depletion. This behaviour is similar to that which has been already observed for $MoTe_{2-x}$ in powder form [12].

3. Theoretical approach

The experimental results reported here can be well fitted using a slightly modified model derived from that developed for p-type $MoTe_{2-x}$ single crystals [9].

3.1. $MoTe_{1.985}$ crystal

At low and medium temperatures, the main contribution to the electrical conductivity and to the TEP comes from electrons in the conduction band where they are expected to interact with both ionized impurities and long wavelength acoustic phonons. They are mainly excited from a bromine narrow level E_D located just below the conduction band. At higher temperatures, the contribution of excited holes in the valence band has to be taken into account where they interact with acoustic vibration modes.

In this simple one-level model, the electrical neutrality is written as: $n = p + N_D^+$ and in the overall range of the temperature investigated, electrical conductivity and thermoelectric power are expressed as follows

$$\sigma = \sigma_p + \sigma_n = \sigma_p + \sigma_{l,i} = \sigma_p + \frac{1}{\rho_l + \rho_i} \tag{1}$$

$$\sigma_l = ne\mu_{l,0}^n\left(\frac{T}{T_0}\right)^{-1.6} \qquad \rho_l = \sigma_l^{-1}$$

$$\sigma_i = ne\mu_{i,0}^n\frac{N_{i,0}}{N_i}\left(\frac{T}{T_0}\right)^{1.5} \qquad \rho_i = \sigma_i^{-1}$$

$$\sigma_p = pe\mu_{l,0}^p\frac{N_{i,0}}{N_i}\left(\frac{T}{T_0}\right)^{1.5}$$

where n, p, N_i are the concentrations in electrons, holes and ionized impurities ($N_i = N_D^+$) respectively. The l 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. Thus, thermoelectric power is expressed as follows

$$S = \frac{\sigma_p S_p + \sigma_{l,i} S_{l,i}}{\sigma} \tag{2}$$

with

$$S_{l,i} = \frac{\rho_l S_l + \rho_i S_i}{\rho_l + \rho_i}, \; S_p = \frac{k_B}{e}[\beta(E_F - E_V) + 4],$$

$$S_l = -\frac{k_B}{e}[\beta(E_C - E_F) + 2]$$

and

$$S_{\mathrm{i}} = -\frac{k_{\mathrm{B}}}{\mathrm{e}}[\beta(E_{\mathrm{C}} - E_{\mathrm{F}}) + 4]$$

where β denotes $1/k_{\mathrm{B}}T$ (k_{B} is the Boltzman constant).

The Hall coefficient R_{H} has been used to scale the carrier concentration. At room temperature, the concentration n being some orders of magnitude larger than the concentration p, the Hall coefficient is given by

$$R_{\mathrm{H}} = \frac{r}{n\mathrm{e}} \tag{3}$$

At this temperature, the scattering of electrons by acoustic phonons being dominant, the constant r has been taken equal to $r = 3\pi/8$. It has been found to be equal to $-6\,\mathrm{cm}^3\,{}^\circ\mathrm{C}^{-1}$ at room temperature.

3.2. MoTe$_{1.97}$ crystal

The variations of $ln\sigma$ and S of MoTe$_{1.97}$ show the existence of a new contribution to transport phenomena. Indeed, the model with one or two extrinsic narrow levels failed in the fit of the TEP curve at low temperatures owing to the low value of S. As suggested in [8], we have supposed that the stoichiometry deviation leads to a broadening of the E_{D} level into a narrow band in which thermally activated hopping conduction mechanisms take place.

Hopping conduction can be written in the general form [13]: $\sigma_{\mathrm{H}} = \sigma_0 \exp[-2\alpha R - \beta W_{\mathrm{H}}(T)]$ in-which α is the damping factor of the wave function, R is the hopping distance between nearest neighbours. $W_{\mathrm{H}}(T)$ which is the hopping energy presents the following T-dependence

$$W_{\mathrm{H}}(T) = \mathscr{W}_{\mathrm{H}}\frac{thx}{x} \tag{4}$$

with $x = \beta(\hbar\omega_0/4)$ and $\hbar\omega_0$ is an optical vibration quantum and $\mathscr{W}_{\mathrm{H}}$ is the hopping energy at the very low temperature limit.

In the non-adiabatic regime, the conductivity σ_{H} due to hopping between nearest neighbour sites is given by: $\sigma_{\mathrm{H}} = N\mathrm{e}\mu_{\mathrm{H}}$

with $N = N_{\mathrm{D}} - N_{\mathrm{D}}^{+}$ and

$$\mu_{\mathrm{H}} = \mu_{\mathrm{H}}^{0}\left(\frac{T_0}{T}\right)^{3/2}(1-c)\exp[-\beta W_{\mathrm{H}}(T)] \tag{5}$$

where c is the relative quantity of the N particles for which hopping can occur: $c = (N_{\mathrm{D}} - N_{\mathrm{D}}^{+})/N_{\mathrm{D}}$
The expression of the associated TEP is given by [14]

$$S = \frac{k_{\mathrm{B}}}{\mathrm{e}}ln\left(\frac{c}{1-c}\right) \tag{6}$$

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

Over the whole temperature range investigated, the electrical conductivity is therefore the summation of the following terms: $\sigma = \sigma_{\mathrm{p}} + \sigma_{\mathrm{l,i}} + \sigma_{\mathrm{H}}$ and $S = (\sigma_{\mathrm{p}}S_{\mathrm{p}} + \sigma_{\mathrm{l,i}}S_{\mathrm{l,i}} + \sigma_{\mathrm{H}}S_{\mathrm{H}})/\sigma$ with

$$\sigma_{\mathrm{l}} = ne\mu_{\mathrm{l,0}}^{n}\left(\frac{T}{T_0}\right)^{-1.9}$$

$$\sigma_{\mathrm{i}} = ne\mu_{\mathrm{i,0}}^{n}\frac{N_{\mathrm{i,0}}}{N_{\mathrm{i}}}\left(\frac{T}{T_0}\right)^{1.5}$$

and

$$S_{\mathrm{l}} = -\frac{k_{\mathrm{B}}}{\mathrm{e}}[\beta(E_{\mathrm{C}} - E_{\mathrm{F}}) + 2.5],$$

$$S_{\mathrm{i}} = -\frac{k_{\mathrm{B}}}{\mathrm{e}}[\beta(E_{\mathrm{C}} - E_{\mathrm{F}}) + 3.8]$$

Using Equation 3, R_{H} has been found to be equal to $-2.3\,\mathrm{cm}^3\,{}^\circ\mathrm{C}^{-1}$ at room temperature.

4. Discussion

It had been shown [8, 9] that the concentration of the acceptor and donor sites both increase as the Te content decreases in the p-type compounds, whereas the $N_{\mathrm{D,L}}/N_{\mathrm{A,L}}$ compensation is close to 0.5. Obviously, the origin of the donor and acceptor levels was lacunary. These semiconductors are weakly compensated and the random potential of acceptor and donor charged centres induces a broadening of the corresponding $E_{\mathrm{A,L}}$ and $E_{\mathrm{D,L}}$ levels into narrow bands. For a high departure from stoichiometry, they participate in the conduction by thermally activated hoppings of small polarons.

For n-type MoTe$_{2-x}$ single crystals, 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 below the bottom of the conduction band and which is issued from the presence of electrically active bromine sites. Almost all the electronic properties of the compounds depend mainly upon the density of carriers of this level. It is found to be very close to the conduction band ($\approx 5\,\mathrm{meV}$ to be compared with the value 9 meV obtained on n-type MoTe$_2$).

The random potential of the charged centres broadens this level into a narrow band in MoTe$_{1.97}$. This band participates in the conduction by thermally activated hopping of small polarons. The value which is found for the hopping mobility ($\approx 0.3\,\mathrm{cm}^2\,\mathrm{V}^{-1}$) is in good agreement with this type of conduction. The optical vibration quantum $\hbar\omega_0$ has been put equal to the usual value 40 meV.

It must be noticed that the lacunar levels, which have been evidenced in [8 and 9], have likely to be taken into account. However, they accept electrons from the bromine level and are, consequently, always filled in the whole temperature range investigated; so, they only act on the conduction mechanisms by partially depleting the bromine level from 0 K. In the case of MoTe$_{1.97}$, the fit shows that these levels accept $4\times10^{17}\,\mathrm{cm}^{-3}$ electrons from the bromine level which leads a marked modification in the hopping conduction mechanism. This value must be compared to that which can be deduced from the results of [8 and 9], i.e. $\approx 10^{18}\,\mathrm{cm}^{-3}$; the difference can be explained under

TABLE I Physical parameters used for the fit

		$MoTe_2$ [7]	$MoTe_{1.985}$	$MoTe_{1.97}$
	E_g (eV)	0.97	0.6	0.5
	N_{V0} (cm^{-3})	3×10^{18}	4.8×10^{18} [8]	4.8×10^{18} [8]
	N_{C0} (cm^{-3})	1.2×10^{19}	1×10^{19}	4.2×10^{18}
	N_D (cm^{-3})	3.3×10^{17}	1.5×10^{18}	7×10^{18}
	$E_C - E_D$ (eV)	9.5×10^{-3}	5×10^{-3}	5×10^{-3}
electrons	μ_l cm^2/Vs	245	75	30
electrons	μ_i cm^2/Vs	720	175	70
hopping	$\mathscr{W}_H$ (eV)	–	–	0.17
hopping	μ_H cm^2/Vs	–	–	0.3

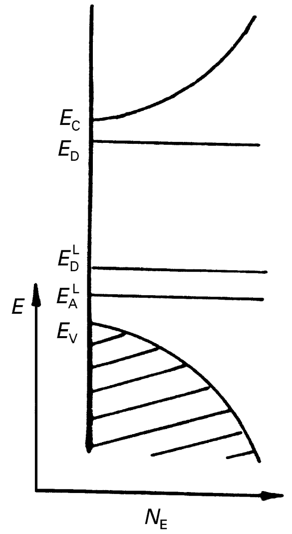

Figure 3 Schematic band model proposed for $MoTe_{1.985}$. The two levels $E_{A,L}$ and $E_{D,L}$ have been shown in refs 8 and 9.

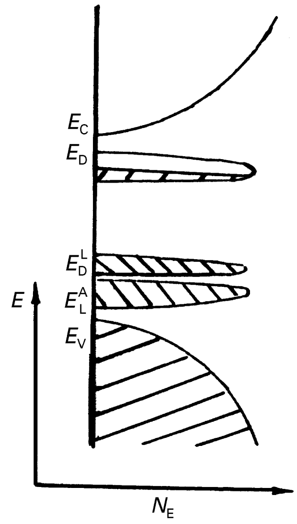

Figure 4 Schematic band model proposed for $MoTe_{1.97}$. The two levels $E_{A,L}$ and $E_{D,L}$ have been shown in refs 8 and 9.

the assumption of a larger compensation $N_{D,L}/N_{A,L}$ in *n*-type $MoTe_{2-x}$.

The decrease of the equivalent density of states of the conduction band of $MoTe_{1.97}$ (4.2×10^{18} to be compared to 1.2×10^{19} for $MoTe_2$ [7]) has to be 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 conduction band must be attributed to the interaction between the conduction band and the narrow band E_D which is very close to E_C ($E_C - E_D = 5$ meV).

Furthermore, the decrease of the energy gap width with tellurium depletion, i.e. 0.6 and 0.5 eV, respectively, at 0 K to be compared with the value 0.97 eV [7], clearly puts in evidence a softening of valence bondings.

The mobility variations calculated at 300 K as a function of the stoichiometry deviation are very characteristic. They put in evidence that the phononic spectrum of the crystal is affected by the Te content decrease. Nevertheless, these values reflect all scattering mechanisms in the conduction band and must not be taken too quantitatively. It must be noticed that the stoichiometry deviation favours the polarization of the material and so, optical modes cannot be neglected. Therefore, the mobility dependence expressed in $T^{-1.6}$ ($T^{-1.9}$) is then, in an approximate way, the total dependence on the mobility results from the two mechanisms (acoustical modes – optical modes).

The values of the physical parameters which give the best fit to the experimental curves are listed in Table I for $MoTe_{1.985}$ and $MoTe_{1.97}$.

Using Equations 1, 2, 4, 5, the theoretical curves are drawn in solid lines in Figs 1a and b and 2a and b whereas the schematic band models which account for all the experimental results are shown in Figs 3 and 4.

5. Conclusion

A bromine donor level has been evidenced just below the bottom of the conduction band of $MoTe_{2-x}$ single crystals prepared by a vapour phase transport method, using bromine as the transport agent. The random potential due to the charged lacunar sites and bromine impurities induces a broadening of this level into a narrow band for $MoTe_{1.97}$ which participates in the conduction in the form of thermally activated hopping.

For the fitting, exponents in mobilities as well as in kinetic terms in the thermoelectric power have not been allowed to depart much from the theoretical values.

The activation energies which have been found are those which can be directly deduced from the experimental curves.

The Hall coefficient, R_H, at room temperature, has been used to scale the carrier concentration and only the mobility and concentration ratios are directly deduced from the fit. Thus, only a reduced number of parameters has been used.

Holes only participate in the conduction in the high temperature range. Their contribution has been fitted by adjusting the gap width value whereas all the parameters which depend upon the valence band have been deduced from other results [8].

To conclude, it must be noticed that the schematic band structure deduced from transport measurements on *n*-type $MoTe_{1.985}$ and $MoTe_{1.97}$ single crystals agrees with the electronic band structure of the group VI transition metal dichalcogenides with trigonal prism coordination [15, 16]. Moreover, we can emphasize that the good agreement between experimental and theoretical results over a wide temperature range, without using any asymptotic behaviour for the calculation of the carrier densities, confirms the validity of the simple model which has been proposed.

References

1. R. SCHOLLHORN, *Physica* **99**B, vol. 6, 1980, 89.
2. J. ROUXEL, "Physics and chemistry of layered materials" (D. Reidel, Dordrecht, 1979) p. 201.
3. G. SCHOLZ, P. JOENSEN, J. M. REYES and R. D. FRINDT, *Physica* **105**B (1981) 214.
4. A. D. YOFFE, *Ann. Chim. Fr.* **7** (1982) 215.
5. H. TRIBUTSCH, *Solar Energy Mater.* **1** (1979) 257.
6. S. CHANDRA and R. K. PANDEY, *Phys. Stat. Solids* (*a*) **72** (1982) 415.
7. A. CONAN, A. BONNET, M. ZOAETER and D. RAMOUL, *ibid.* (*b*) **124** (1984) 403.
8. A. BONNET, A. CONAN, M. SPIESSER and M. ZOAETER, *J. Phys.* (*France*) **49** (1988) 803.
9. A. BONNET, A. CONAN, Y. TREGOUET, M. ZOAETER and M. MORSLI, *J. Phys. I* (*France*) **1** (1991) 779.
10. M. SPIESSER and J. ROUXEL, *C.R. Acad. Sci. II* **328** (1983) 55.
11. A. BONNET, P. SAID and A. CONAN, *Rev. Phys. Appl.* **17** (1982) 701.
12. A.CONAN, G. GOUREAUX and M. ZOAETER, *J. Phys. Chem. Sol.* **36** (1975) 315.
13. A. L. EFROS and B. I. SCHKLOVSKIJ, "*Electron Interaction in Disordered Systems*", edited by A. L. Efros and M. Pollak (Elsevier Science Publishers, Amsterdam, 1985).
14. R. HEIKES, in "Bull International Conference on Materials", edited by E. R. Schartz (Gordon and Breach, New York, 1974) p. 180.
15. L. F. MATTHEISS, *Phys. Rev. B* **8** (1973) 3719.
16. I. T. McGOVERN and R. H. WILLIAMS, *Nuovo Cimento* **38B** (1977) 2.

Received 21 August 1995
and accepted 21 October 1996