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2004 J. Phys.: Condens. Matter 16 L359

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LETTER TO THE EDITOR

Observation of a semimetal–semiconductor phase transition in the intermetallic ZrTe_5

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Received 16 June 2004

Published 16 July 2004

Online at stacks.iop.org/JPhysCM/16/L359

doi:10.1088/0953-8984/16/30/L02

Abstract

Temperature dependent high-resolution angle-resolved photoelectron spectroscopy has been performed on the quasi-two-dimensional compound ZrTe_5 , a metal at low temperatures ($T \leq 4.2$ K) that exhibits a maximum resistivity at a temperature (T_c), concomitant with a sign change of the thermopower. A semiconducting gap has been observed in the photoemission spectra, where the valence band maximum shifts upward from 82 meV (75 K) to 40 meV (170 K) as a function of temperature. The band shifts are accompanied by small band distortions. Based on the photoemission experiments, in conjunction with the metallic character of ZrTe_5 at low temperatures, we have modelled the thermopower of ZrTe_5 by treating it as a metal at low temperatures and a semiconductor at elevated temperatures.

Low-dimensional (2D) and quasi-low-dimension materials have received considerable attention due to their tendency to exhibit novel behaviour such as superconductivity [1, 2], colossal magnetoresistance (CMR) [3, 4], and charge density wave (CDW) formation [5–7], to name a few. The aforementioned behaviour is typically accompanied by a metal–nonmetal or semimetal–nonmetal transition associated with either the formation of a gap [1, 2, 4] or changes in the width of the gap [3, 4]. Low-dimensional systems are inherently unstable due to correlation and exchange effects, and consequently they exhibit structural instabilities such as Jahn–Teller distortions [4] or CDW distortions [5–7]. One class of these exotic materials is the pentatellurides (ZrTe_5 and HfTe_5), which exhibit anomalous transport properties attributed to their quasi-two-dimensional structure [8, 9]. The structure of the pentatellurides consists of zigzag chains of Te atoms along the a -axis that link prismatic chains of ZrTe_6 along the

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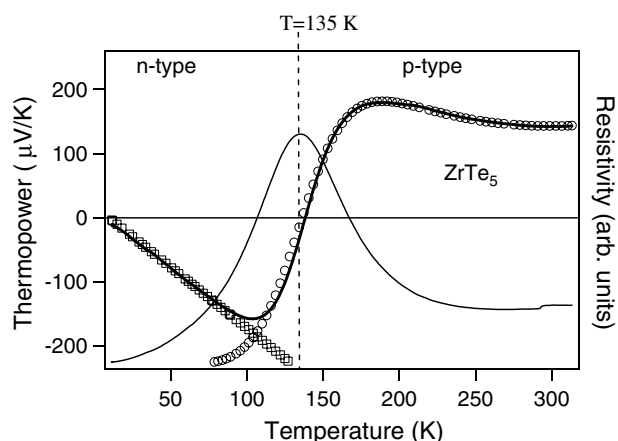


Figure 1. The temperature dependent thermopower (bold curve) and resistivity (thin curve) of ZrTe_5 , where the resistivity has been normalized to $\rho(273 \text{ K})$. The open squares and circles are the fits to the thermopower using equations (2) and (4), respectively.

c -axis, which together form 2D planes weakly bonded via van der Waals forces along the b -axis. This structure belongs to the $Cmcm$ (D_{2h}^{17}) space group. Presented in figure 1 is the bulk resistivity and thermopower of ZrTe_5 as a function of temperature. The growth and experimental procedures for measuring the resistivity and thermopower are discussed in detail elsewhere [10]. Summarizing figure 1, the resistivity of ZrTe_5 increases with temperature, consistent with metallic behaviour, until it peaks at $T \simeq 135 \text{ K}$, at which point the resistivity begins to decrease, reminiscent of a semiconductor. The room temperature resistivity of ZrTe_5 is of the order $0.7 \text{ m}\Omega \text{ cm}$ [11], which suggests that it is a poor semimetal, at best. This paradoxical behaviour of ZrTe_5 has eluded explanation for nearly 20 years.

Since the mid-1980s it has been hypothesized that the anomalous peaks in the resistivities (figure 1) of this class of materials were signatures of charge density waves. The rationale behind this hypothesis is based, in part, on the similarities between the crystal structures of the pentatellurides and NbSe_3 , a known CDW system that also possesses an anomalous peak in its resistivity. A further suggestion of CDW formation is the change in the sign of the thermopowers of the pentatellurides, i.e. from electron carriers to hole carriers, at a temperature which corresponds to the anomalies in their respective resistivities [11, 12]. However, attempts to observe structural distortions in the pentatellurides to verify the formation of CDWs have been unsuccessful [13]. The only information on the electronic structure of ZrTe_5 has come indirectly from Shubnikov–de Haas (SdH) measurements acquired between 1.3 and 4.2 K [11, 12], which suggested that the valence band structure in the vicinity of the Fermi level consists of three bands, two electron bands and one hole band. The SdH measurements of ZrTe_5 are in reasonable agreement with band structure calculations of ZrTe_5 by Whangbo *et al* [14]. In order to shed new light on the question of CDW formation in the pentatellurides, we have measured the band structure of ZrTe_5 as a function of temperature using high-resolution angle-resolved photoelectron spectroscopy (APRES).

The angle-resolved photoemission studies were performed at the Synchrotron Radiation Center in Stoughton, WI, on the Ames-Montana beamline using a 50 mm hemispherical analyser and on the 4 m normal incidence monochromator (NIM) using a Scienta SES 200 multichannel analyser. For the sack of brevity, only spectra acquired with the Scienta analyser on the 4 m NIM beamline are presented. The samples were ribbon-like, where the long

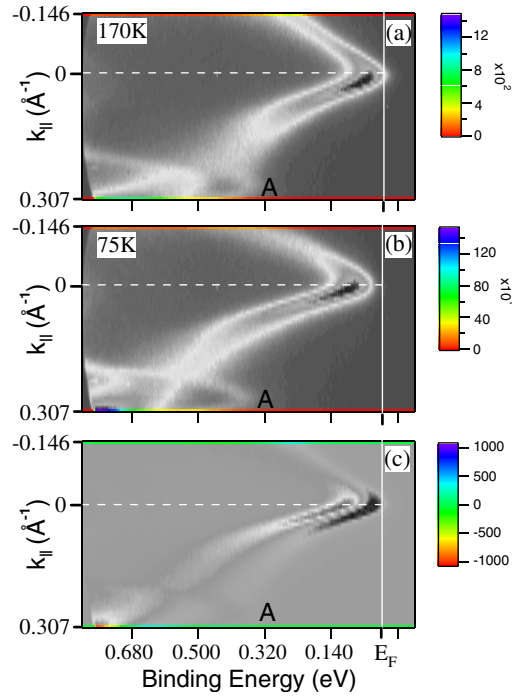


Figure 2. Intensity maps of the density of states of ZrTe_5 acquired along the Γ -X high symmetry direction for (a) $T = 170$ K and (b) $T = 75$ K, and (c) an intensity difference map between the maps in (a) and (b).

(This figure is in colour only in the electronic version)

axis was the Zr chain (a) axis. The visual orientation was confirmed by *ex situ* Laue and *in situ* symmetries of the band dispersions. The samples were initially cooled to 20 K, then raised to 170 K and cleaved *in situ* exposing the a - c plane. The angular resolution of the Scienta analyser is $\pm 0.25^\circ$, which corresponds to a reciprocal space resolution of 0.010 \AA^{-1} ; 1.25% of π/a or 4.25% of π/c . Spectra were acquired along the Γ -X (a -axis in [11]) and Γ -Z (c -axis in [11]) directions, respectively. Photon energy dependence of the ZrTe_5 bands at normal emission indicated dispersion perpendicular to the a - c plane, which is attributed to the weak bonding along the b -axis. From a survey of the photon energy dependence of the ZrTe_5 bands, $h\nu = 22$ eV corresponded to being the extreme of the perpendicular dispersion. Consequently, all spectra were acquired at a photon energy of 22 eV, which corresponded to an energy resolution of 20 meV.

Presented in figure 2 are normalized two-dimensional intensity maps of the Fermi surface of ZrTe_5 along the Γ -X high symmetry line at (a) 170 K and (b) 75 K. Figure 2(c) is an intensity difference map between figures 2(a) and (b). The band structure of ZrTe_5 in the vicinity of the Fermi level consists of two downward dispersing bands that are nearly degenerate ($\Delta E \simeq 40$ meV), consistent with tight binding calculations of ZrTe_5 [14]. At 170 K the valence band maximum (VBM) is at a binding energy of 40 meV, but it shifts downward to 82 meV at 75 K, or $\Delta_{\text{Gap}} = 42$ meV. Equivalent band gaps and band shifts were observed for the Γ -Z high symmetry direction (not shown). Note, the band labelled A in figures 2(a) and (b) is absent from the difference map in figure 2(c), indicating that the binding energy of this band is temperature independent. Based on the SdH measurements [11, 12] and the

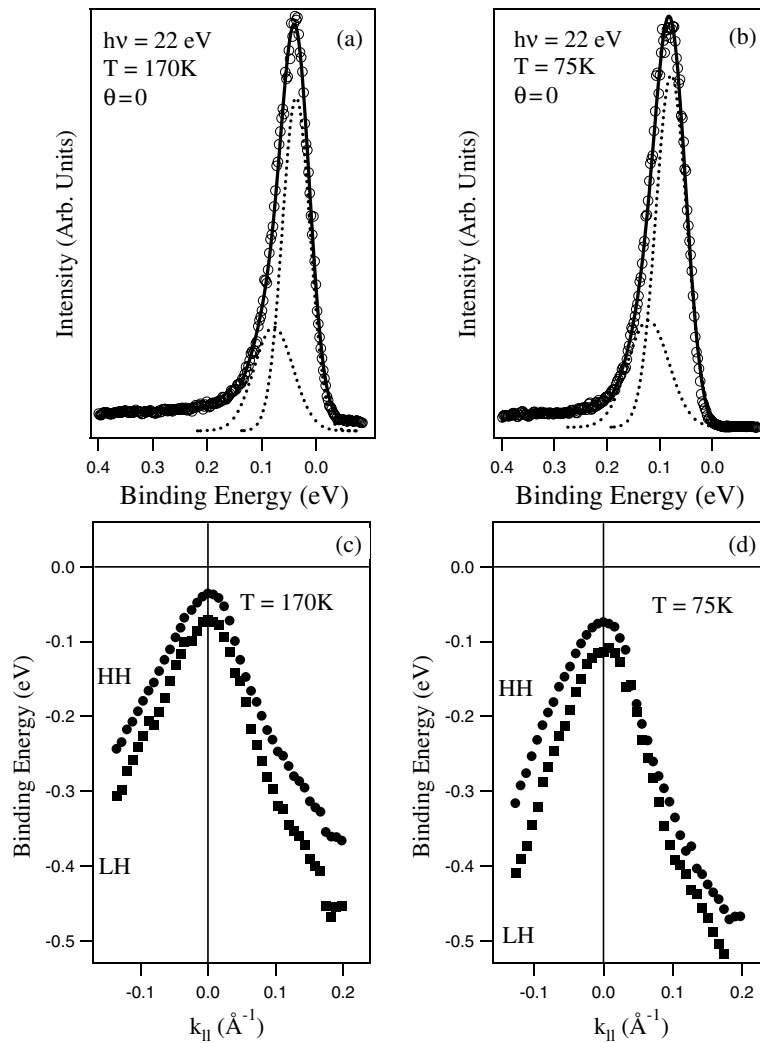


Figure 3. APRES spectrum of ZrTe₅ acquired at Γ from (a) figure 2(a) for $T = 170$ K and (b) figure 2(b) for $T = 75$ K, and the experimental band dispersions of ZrTe₅ for (c) $T = 170$ K and (d) $T = 75$ K. In (a) and (b) the symbols are the experimental data, the solid curves are the fits, and the dashed curves are the deconvolutions of the fits into individual bands.

band structure calculations [14] of ZrTe₅, the spectra in figure 2 have been fitted with two Lorentzians convoluted with Gaussians. Examples of the fits are presented in figures 3(a) and (b). The temperature dependent band dispersions of ZrTe₅, based on the deconvolutions, are displayed in figures 3(c) and (d), respectively.

The downward dispersion of the ZrTe₅ bands in figures 2 and 3 is consistent with the heavy hole (HH) and the light hole (LH) bands typical of a semiconductor [15], and when taken in conjunction with the persistence of a band gap at 20 K, indicates that ZrTe₅ is a semiconductor for $T \geq 20$ K, as opposed to a semimetal. On the other hand, since the SdH effect requires Fermi level crossings, ZrTe₅ must be metallic for $T \leq 4.2$ K [11]. Based on the ARPES and SdH measurements, we must conclude that ZrTe₅ exhibits a metal–semiconductor phase

transition for $4.2 \text{ K} < T < 20 \text{ K}$. Furthermore, the APRES and SdH measurements [11, 12], in agreement with the band structure calculations [14], indicate that ZrTe_5 is a direct band gap semiconductor for $T \geq 20 \text{ K}$. It is worth noting that the band structure of ZrTe_5 is reminiscent of $\alpha\text{-Sn}$ (zero band gap) and HgTe (negative bandgap) [15].

Whangbo *et al* compared the band structure of a 2D ZrTe_5 slab and 3D ZrTe_5 [14] in order to evaluate the effects of interlayer interactions between a - c planes on the band structure. For the 2D slab, the band structure in the vicinity of the Fermi level consists of two highly dispersive bands, one downward dispersing hole band \underline{a} (occupied) and one upward dispersing electron band \underline{b} (unoccupied), respectively, separated by a 50 meV band gap. Consequently, the isolated 2D ZrTe_5 slab is a semiconductor. The \underline{a} -band originates from the Te $5p_y$ orbitals of the prismatic chains in the a - c plane and the \underline{b} -band originates from the Te $5p_z$ orbitals of the zigzag chains in the a - c plane.

For 3D ZrTe_5 Whangbo *et al* found that interplane interactions between the a - c planes causes doubling of the \underline{a} and \underline{b} bands. The 3D ZrTe_5 band structure in the vicinity of the Fermi level consists of two downward dispersing bands, a_1 and a_2 , and two upward dispersing band, b_1 and b_2 , respectively. An additional effect of the interplane interactions is the occupation of the b_1 band due to overlap with the a_2 band, i.e. a_2 and b_1 exhibit Fermi level crossings, while a_1 and b_2 do not cross the Fermi level. In contrast to the 2D ZrTe_5 slab, 3D ZrTe_5 is metallic and the metallicity arises from interlayer interactions.

The 3D valence band structure of ZrTe_5 predicted by Whangbo *et al* [14] is in excellent agreement with the ARPES spectra in figures 2 and 3, with the exclusion of the predicted Fermi level crossings. Conversely, the 50 meV band gap predicted for the 2D ZrTe_5 slab is consistent with the minimum gap of 40 meV (170 K) observed with ARPES (figures 2 and 3). In contrast, the SdH measurements indicate a metallic phase for ZrTe_5 for $T < 4.2 \text{ K}$, in agreement with the tight binding calculations of 3D ZrTe_5 by Whangbo *et al* [14]. However, the SdH measurements observed three band crossings, as opposed to the two predicted for 3D ZrTe_5 [14]. While the ground state 3D tight binding calculations of ZrTe_5 is flawed, it does capture the basics of ZrTe_5 . Namely, at low temperatures ZrTe_5 is metallic and the valence band structure in the vicinity of the Fermi level consists of two downward dispersing hole-like bands. The significance of the calculations of Whangbo *et al* [14] is that the semimetallic properties of ZrTe_5 for $T < 4.2 \text{ K}$ arise from interplane interactions as opposed to intraplane interactions. However, the existence of a band gap for ZrTe_5 for $T \geq 20 \text{ K}$ indicates that the interplane interactions at these temperatures are much weaker than those in the ground state calculation of 3D ZrTe_5 [14].

Since ZrTe_5 has an even number of electrons per unit cell, at the metal–semiconductor transition it must be an intrinsic semiconductor, i.e. the chemical potential is midgap. The upward shift of the valence band maximum of ZrTe_5 from 82 meV at 75 K to 40 meV at 170 K is consistent with an intrinsic semiconductor. Specifically, the chemical potential for an intrinsic semiconductor will shift downward towards the VBM as a function of temperature, provided the hole effective mass (m_h) is less than the electron effective mass (m_e) [16]. A ratio of $m_h/m_e > 1$ is consistent with the positive sign of the thermopower in figure 1 for $T > 135 \text{ K}$. The 3D character of the bands of ZrTe_5 precluded us from performing constant initial state experiments and therefore we cannot comment on the role of final state effects on the band structure. However, invoking final state effects to explain the temperature dependent valence band shifts is inconsistent with the bulk transport in figure 1.

If taken alone, the band structure at $T > 135 \text{ K}$ in figure 2(a) could be argued to be reminiscent of a semimetal. However, the transport data in figure 1 do not support this conclusion. In order to resolve this contradiction the unoccupied density states need to be examined. In the absence and difficulties of acquiring this data, we hypothesize that the

upward shift of the occupied bands is accompanied by an equivalent upward shift of the lowest unoccupied band. If this is indeed the case then the presence of occupied states at the chemical potential could not be taken as an indication of a semimetal state since a gap remains, i.e. a semiconducting phase. Consequently, it is concluded that at $T > 135$ K ZrTe₅ is a p-type semiconductor.

Based on results of the SdH measurements [11] and this photoemission study of ZrTe₅, we have developed a simple model to explain the temperature dependence of the thermopower in figure 1. Classically, the temperature dependence of the thermopower (S) of a metal can be expressed by the Mott–Jones equation:

$$S(T) = -\frac{\pi^2 k_B^2 T}{3e E_{FO}} a, \quad (1)$$

where k_B is the Boltzmann constant, T is temperature, e is the electron charge, E_{FO} is the Fermi energy at $T = 0$ K, and a is a numerical constant that accounts for changes in electron transport, such as the mean free path of the electron, as a function of electron kinetic energy [16]. Since electron conduction is mediated through scattering by phonons, impurities and crystal defects, a should be proportional to the mean free path of the conduction electrons (l_s), assuming a simple Drude model of scattering. Therefore, we can rewrite equation (1) as

$$S(T) = -\left[\frac{\pi^2 k_B^2 T}{3e E_{FO}}\right] [Cl_s], \quad (2)$$

where C is a constant with units of reciprocal length. Using equation (2) we have fitted the low temperature regime of the thermopower of ZrTe₅ in figure 1. We see that this simple model begins to fail around 90 K, which we attribute to changes in the density of states at the Fermi level corresponding to the onset of the transition to the semiconducting phase.

In order to model the transport in the semiconducting phase we replace l_s in equation (2) with $v_d \tau$, where v_d is the drift velocity of a hole and τ is the mean free time between collisions. From the hole conductivity (σ) for a semiconductor we can extract τ :

$$\tau_h = \left[\frac{m_h^* \sigma(T)}{e^2 N}\right] \left[\alpha e^{\frac{E_g}{2k_B T}} + e^{-\frac{E_g}{2k_B T}}\right]^{-1}, \quad (3)$$

where m_h^* is the hole effective mass, $\sigma(T)$ is the temperature dependent conductivity, N is the hole concentration, which we have assumed does not change with temperature, α is the ratio of the electron mobility to the hole mobility, and E_g is the energy gap of the semiconductor. Within a first approximation, we assume that $\sigma(T) = aT$, which from examination of figure 1 we see is reasonable for $135 \text{ K} < T < 170 \text{ K}$. Upon making this substitution into equation (2) we arrive at the following relationship for the thermopower:

$$\begin{aligned} S(T) &= -\left[\frac{C \pi^2 m_h^* k_B^2 v_d a T^2}{3e^3 N E_{FO}}\right] \left[\alpha e^{\frac{E_g}{2k_B T}} + e^{-\frac{E_g}{2k_B T}}\right]^{-1} \\ &= -DT^2 \left[\alpha e^{\frac{E_g}{2k_B T}} + e^{-\frac{E_g}{2k_B T}}\right]^{-1}, \end{aligned} \quad (4)$$

where $D = \left[\frac{C \pi^2 m_h^* k_B^2 v_d a}{3e^3 N E_{FO}}\right]$. The linear region of the thermopower ($135 \text{ K} < T < 170 \text{ K}$) in figure 1 was fitted with equation (4) and then calculated for $75 \text{ K} < T < 320 \text{ K}$, where D , α and E_g were the free parameters. From examination of figure 1 we see that a surprisingly good fit of the thermopower is achieved for $T > 120 \text{ K}$. We attribute the failure of this model at $T < 120 \text{ K}$ to temperature dependent changes in phonon scattering and the phase transition to the metallic phase. The theoretical gap for the semiconducting phase of ZrTe₅ based on the fit is 108 meV, which only differs, approximately, by a factor of two from the minimum band

gap of 40 meV, as determined by ARPES, and the theoretical gap of 50 meV for the 2D ZrTe₅ slab [14].

In conclusion, we have used the technique of high-resolution angle-resolved photoelectron spectroscopy to study the temperature dependent electronic structure of ZrTe₅. In the temperature range $20 \text{ K} \leq T \leq 170 \text{ K}$ a band gap was observed, indicative of a semiconducting phase. In addition, the chemical potential was observed to shift downwards with temperature, consistent with an intrinsic semiconductor. Since ZrTe₅ is metallic for $T \leq 4.5 \text{ K}$, as determined from the Shubnikov–de Haas effect, we have concluded that a metal–semiconductor phase transition occurs for $4.2 \text{ K} < T < 20 \text{ K}$. While we cannot exclude charge density wave formation for $T < 20 \text{ K}$, the lack of experimental evidence argues against this explanation for the metal–semiconductor transition. However, our observations suggest that it is a reduction in interplane interactions between the *a*–*c* planes of ZrTe₅ that is responsible for the transition. A thorough study of the temperature dependent phonon density of states would likely shed much needed light on the origin of the phase transition.

The Synchrotron Radiation Center, University of Wisconsin-Madison, is supported by the NSF under Award No DMR-0084402. The Ames Laboratory is supported by the USDOE under Contract No W-7405-ENG-82. The authors would like to acknowledge the valuable assistance of Drs Hartmut Hochst and Kyle Altmann.

References

- [1] Norman M R, Ding H, Randeria M, Campuzano J C, Yokoya T, Takeuchi T, Mochiku T, Kadowaki K, Guptasarma P and Hinks D G 1998 *Nature* **392** 157
- [2] Allen J W, Olson C G, Maple M B, Kang J-S, Liu L Z, Park J-H, Anderson R O, Ellis W P, Markert J T, Dalichaouch Y and Liu R 1990 *Phys. Rev. Lett.* **64** 595
- [3] McIlroy D N, Zhang J, Liou S-H and Dowben P A 1995 *Phys. Lett. A* **207** 367
- [4] Park J-H, Chen C T, Cheong S-W, Bao W, Meigs G, Chakarian V and Idzerda Y U 1996 *Phys. Rev. Lett.* **76** 4215
- [5] Gweon G-H, Denlinger J D, Clack J A, Allen J W, Olson C G, DiMasi E, Aronson M C, Foran B and Lee S 1998 *Phys. Rev. Lett.* **81** 886
- [6] Nakamura M, Sekiyama A, Namatame H, Fujimori A, Yoshihara H, Ohtani T, Misu A and Takano M 1994 *Phys. Rev. B* **49** 16191
- [7] Dardel B, Grioni M, Malterre D, Weibel P and Baer Y 1992 *Phys. Rev. B* **45** 1462
- [8] Wieting T J, Gubser D U, Wolf S A and Levy F 1980 *Bull. Am. Phys. Soc.* **25** 340
- [9] Okada S, Sambongi T and Ido M 1980 *J. Phys. Soc. Japan* **49** 839
- [10] Littleton R T, Tritt T M, Feger C R, Kolis J, Wilson M L, Marone M, Payne J, Verebeli D and Levy F 1998 *Appl. Phys. Lett.* **72** 2056
- [11] Kamm G N, Gillespie D J, Ehrlich A C, Wieting T J and Levy F 1985 *Phys. Rev. B* **31** 7617
- [12] Kamm G N, Gillespie D J, Ehrlich A C, Peebles D L and Levy F 1987 *Phys. Rev. B* **35** 1223
- [13] DiSalvo F J, Fleming R M and Waczak J V 1981 *Phys. Rev. B* **24** 2935
- [14] Whangbo M-H, DiSalvo F J and Fleming R M 1982 *Phys. Rev. B* **26** 687
- [15] Cohen M L and Chelikowsky J R 1989 *Electronic Structure and Optical Properties of Semiconductors* (New York: Springer)
- [16] Kasap S O 2000 *Principles of Electrical Engineering Materials and Devices* (Boston, MA: McGraw-Hill)