Available online at www.sciencedirect.com

ScienceDirect

C. R. Physique 8 (2007) 942–947

COMPTES RENDUS PHYSIQUE

http://france.elsevier.com/direct/COMREN/

Physics/Solids, fluids: magnetic and electrical properties

Effect of the high magnetic field on the localization length in n-type Cooper Indium diselenide

Lahcen Essaleh [a,*], Syed M. Wasim [b], Jean Galibert [c]

[a] *Laboratoire de matière condensée et nanostructures (LMCN), université Cadi-Ayyad, faculté des sciences et techniques, département de physique, Guéliz, BP 549, Marrakech, Morocco*

[b] *Centro de Estudios de Semiconductores, Facultad de Ciencias, Universidad de Los Andes, Merida 5101, Venezuela*

[c] *Laboratoire national des champs magnétique pulsés, 143, avenue de Rangueil, BP 4245, 31432, Toulouse cedex 4, France*

Received 9 May 2007; accepted 5 July 2007

Available online 4 September 2007

Presented by Jacques Villain

Abstract

Variable range hopping conduction of the Mott type, where the magnetoresistance follows the relation $\rho(B) = \rho_o \exp[T_o(B)/T]^{1/4}$, is observed in n-type $CuInSe_2$ below 20 K at different magnetic field values up to 35 T. The field dependence of the localization temperature T_o and localization length ξ can be explained with the existing theoretical models but only up to 10 T. In the high field regime, above 10 T, the magnetoresistance shows a tendency to saturate. However, excellent agreement with the theory of the variation of the hopping parameters T_o and ξ with B is found up to 35 T from the analysis of the interpolated magnetoresistance data obtained from the linearly extrapolated plot of $\mathrm{Ln}\,\rho(B)/\rho(0)$ against $B^{1/3}$. This suggests that the departure of T_o and ξ from the expected variation with B above 10 T is due to the effect of saturation of the magnetoresistance whose origin is not yet clear. ***To cite this article: L. Essaleh et al., C. R. Physique 8 (2007).***

Résumé

Effet du champ magnétique sur la longueur de localisation dans n-type $CuInSe_2$. La conduction par saut à distance variable de type Mott où la magnétorsistance suit la relation $\rho(B) = \rho_o \exp[T_o(B)/T]^{1/4}$, est observée dans n-$CuInSe_2$ en dessous de 20 K pour un champ magnétique B allant jusqu'à 35 T. L'effet de B sut la température caractéristique T_o et sur la longueur de localisation ξ est expliqué à l'aide des modèles théoriques existants mais pour $B < 10$ T. Pour $B > 10$ T, la magnétorésistance présente un comportement de saturation. Cependant, les variations de T_o et ξ avec B sont en accord avec la théorie lorsqu'on considère les données obtenues par extrapolation des courbes $\mathrm{Ln}\,\rho(B)/\rho(0)$ en fonction de $B^{1/3}$. Ceci suggère que le désaccord observé au dessus de 10 T est lié à la saturation de la magnétoprésistance. L'origine de cette saturation n'est pas encore claire. ***Pour citer cet article : L. Essaleh et al., C. R. Physique 8 (2007).***

Keywords: Semiconductor; Variable range hopping; Magnetoresistance

Mots-clés : Semi-conducteur ; Saut à distance variable ; Magnétorsistance

* Corresponding author.
E-mail addresses: lessaleh@yahoo.com, lessaleh@fstg-marrakech.ac.ma (L. Essaleh).

1631-0705/$ – see front matter
doi:10.1016/j.crhy.2007.07.001

1. Introduction

The ternary compounds of the Cu-III-VI_2 family, which have chalcopyrite structure with space group $I\bar{4}2d$, continue to be promising materials for opto-electronic and photovoltaic devices [1,2]. In addition, these compounds are also very useful in understanding and extending the basic physical concepts of the electrical conduction mechanisms involved in elemental and binary compound semiconductors. $CuInSe_2$ (CIS) is one such compound. Solar cells with efficiency around 20% have been fabricated with the alloys of $CuIn_{1-x}Ga_xSe_2$ [3].

The electrical conductivity of n-type CIS down to liquid helium temperature in the variable range hopping (VRH) of Mott type and metallic conduction regimes have been studied extensively [4–6]. Experimental efforts have been concentrated mainly to study in the low temperature range the magnetic field and temperature dependence of both negative magnetoresistance (NMR) observed at lower fields and positive magnetoresistance (PMR), observed at higher fields. Strong evidence supporting the validity of the quantum interference model, that explains the origin of NMR in very low fields, has been observed [7]. At higher fields, above the critical field B_c that defines the crossover from the weak to strong field regime, the PMR can be explained quite satisfactorily by the expression proposed by Efros and Shklovskii [8] that takes into account the shrinkage of the wave functions. It is also observed that at low temperatures the magnetoresistance at very high fields ($B \gg B_c$) tends to saturate [4]. This saturation of the magnetoresistance, whose origin is not yet clear, has strong effect on the magnetic field dependence of the localization length ξ.

Continuing our earlier works on Mott type VRH conduction in n-CIS [4–7], we report in the present Note a detailed analysis of high field magnetoresistance data up to 35 T in the temperature range between 1.9 and 20 K. The effect of saturation of the magnetoresistance on the localization length is discussed. The results are compared with the existing theoretical models.

2. Experimental methods

The samples used in the present work were cut from the ingot that was grown by the vertical Bridgman technique using elements of at least 5 N purity. A slight excess of indium in the stoichiometry was used to produce n-type CIS. Electrical measurements were made with current flowing either perpendicular or along the $\langle 112 \rangle$ axis. The samples are accordingly named CIS1 and CIS2, respectively. Other experimental details about the sample preparation and contacts are reported elsewhere [9].

3. Experimental results and discussion

From the temperature dependence of the Hall coefficient of CIS1 and CIS2 samples, the donor concentration N_D, the compensating acceptor concentration N_A and the activation energy E_D were calculated using the approach of Emelyanenko et al. [10] for the two bands model. These are, respectively, 6.82×10^{16} cm^{-3}, 1.82×10^{16} cm^{-3} and 6.50 meV for CIS1, and 4.74×10^{16} cm^{-3}, 7.40×10^{15} cm^{-3} and 8.64 meV for CIS2. With the dielectric constant $\varepsilon_o = 9.3$, the electron effective mass $m_e^* = 0.09 m_e$, the Bohr radius is calculated to be $a = 54.3$ Å. The critical concentration n_c, calculated from the Mott's criterion $n_c a^{1/3} \approx 0.25$ for the metal–insulator (MI) transition, is found to be 9.80×10^{16} cm^{-3}. This indicates that both samples are in the strong localization regime on the insulator side of the MI transition.

The logarithmic variation of the electrical resistivity ρ of a representative sample CIS1 of n-$CuInSe_2$ is plotted in Fig. 1 as a function of $T^{-1/4}$ at different values of the magnetic field B up to 35 T. The straight lines, in the temperature range between 1.9 and 20 K, agree with Mott's law $\rho = \rho_o \exp[T_o(B)/T]^{1/4}$ for the VRH conduction in the impurity band when the density of the localized states at the Fermi level is constant. The values of the pre-exponential factor ρ_o and the localization temperature T_o, obtained from the least-square fit to the experimental data of Fig. 1, are given in Table 1. Their variations, as a function of B, are shown in curve (a) of Fig. 2.

The localization temperature T_o can be expressed in terms of the localized density of states $N(E_F)$ at the Fermi level and the localization length ξ by the relation [8]

$$T_o = \frac{\beta}{k_B N(E_F)\xi^3} \tag{1}$$

where β is a numerical coefficient and k_B is the Boltzmann constant.

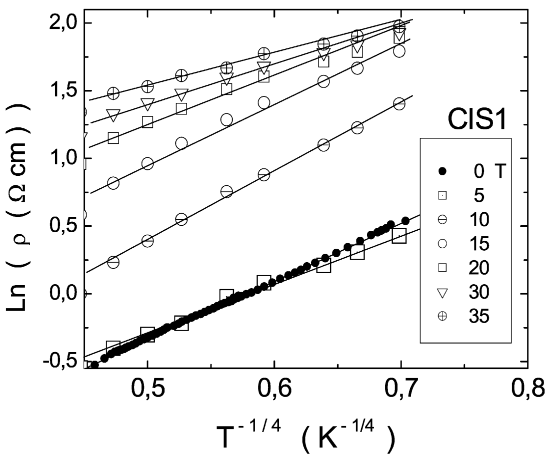

Fig. 1. The variation of the electrical resistivity ρ of a representative sample CIS1 as a function of temperature in the range 1.9–20 K at different fixed magnetic field values up to 35 T. The straight lines show the linear behavior.

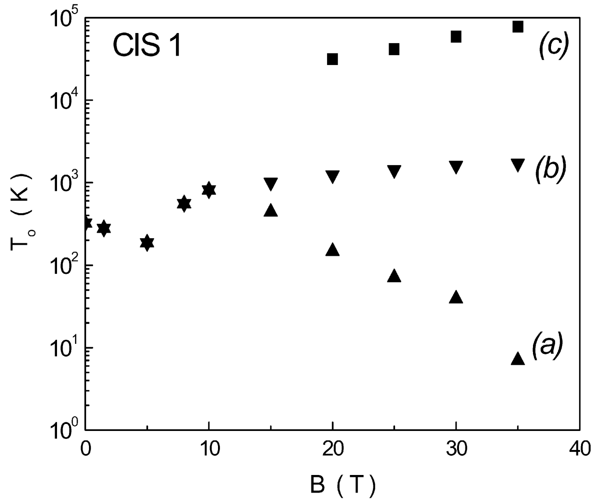

Fig. 2. The variation of the localization temperature T_o as a function of magnetic field. The values T_o obtained from the fit by the Mott's law $\rho \propto \exp[T_o/T]^{1/4}$ to the experimental data are shown in curve (a) and those obtained from extrapolation up to 35 T of $\mathrm{Ln}\,\rho(B) \propto B^{1/3}$ data in curve (b). The values of T_o calculated with the method of Tokumoto et al. [11] are represented in curve (c).

Table 1
Values of the parameters ρ_o and T_o in Mott's law $\rho = \rho_o \exp[T_o(B)/T]^{1/4}$ at different magnetic fields, obtained from a theoretical fit to the experimental data in the temperature range 4.2–20 K

B (T)	0	1.5	5	8	10	15	20	30	35
ρ_o (Ω cm) (×10^{-4})	866	925	1172	963	1000	2587	6062	12 484	14 044
$\Delta\rho_o$ (Ω cm) (×10^{-4})	70	10	70	63	100	300	700	1100	900
T_o (K)	324	278	187	557	813	440	147	39	7
ΔT_o (K)	4	8	21	50	60	55	35	9	0.9

It is assumed, for the analysis of the data, that $N(E_F)$ does not vary with the magnetic field and the variation of T_o, depending on Eq. (1), is entirely due to the change in the localization length ξ. As observed in curve (a) of Fig. 2, the field dependence of T_o can be separated into three well-defined regions that are between 0 to 5 T, 5 to 10 T and 10 to 35 T. For the analysis, these ranges will be referred to as I, II and III, respectively. In the region I of low field, where NMR is observed (see Ref. [7]), T_o decreases with the increases of B. This implies, from Eq. (1), that the localization length at first increases with the magnetic field. This increase of ξ with B is associated with the magnetic field induced delocalization effect that originates NMR. In the range II, above 5 T, the shrinkage of the wave functions of the impurity states is expected to decrease the localization length ξ and thereby increase T_o. However, at higher field above 10 T, in range III, T_o, as in range I, decreases with B. This abnormal behavior is in contradiction with the theoretical predictions [8,11] of the magnetic field dependence of the localization temperature. In the high field region, above the critical field B_c, when the magnetoresistance is completely positive, the localization length ξ decreases, T_o increases and tends to saturate at very high fields [11]. The observed anomaly of T_o, decreasing with B in range III is, according to our interpretation, related to the fact that the magnetoresistance saturates below 10 K and above 10 T. This can be observed clearly in Fig. 3. A similar behavior has also been reported in other works [12–14]. The physical origin of this saturation is not yet clear.

It is shown that at fields greater than B_c, the logarithmic variation of the magnetoresistance in two samples CIS1 and CIS2 of n-type $CuInSe_2$ [4] is proportional to $B^{1/3}$. This is in agreement with the theory of Efros and Shklovskii [8]. The expected magnetoresistance, in the absence of the effect of saturation, is obtained from the experimental data in the high magnetic field region from the linear part of Ln $\rho(B)/\rho(0)$ versus $B^{1/3}$ curves at different temperatures that are extrapolated up to 35 T. This is shown for two representative temperatures at 1.9 and 4.2 K in Fig. 3 by dotted

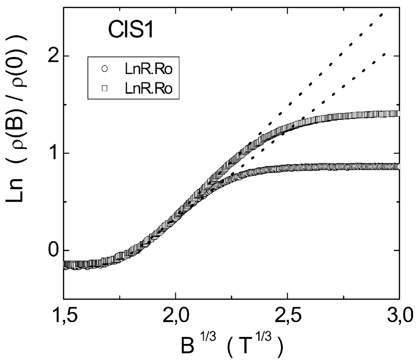

Fig. 3. A plot of $\ln[\rho(B)/\rho(0)]$ of a representative sample CIS1 as a function of $B^{1/3}$ at 1.9 and 4.2 K. The dotted lines show the linear behavior.

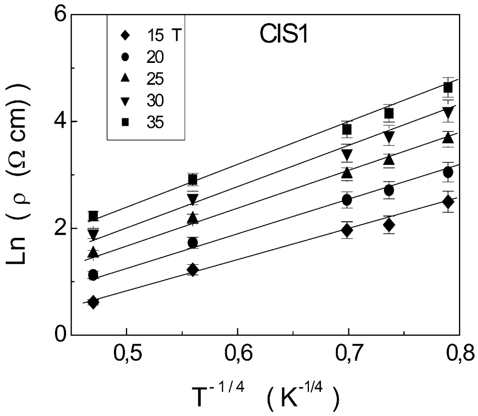

Fig. 4. The variation of $\ln\rho$ of a representative sample CIS1 as a function of $T^{-1/4}$ at different fixed magnetic fields. The data are obtained from extrapolating the $\mathrm{Ln}\,\rho(B) \propto B^{1/3}$ curves up to 35 T. The straight lines show the linear behavior.

lines. The values of Ln ρ, thus obtained, are plotted in Fig. 4 as a function of $T^{-1/4}$ for different values of B up to 35 T. The observed linear dependence at fixed B indicates that the electrical resistivity follows Mott's law. It can also be noticed that the slope of the corresponding straight line increases with increasing B. This means that, contrary to what is shown in curve a of Fig. 2, T_o increases with B if the effect of saturation were not present and would thus be consistent with the decrease of the localization length ξ with the increase of the magnetic field. This is shown in curve (b) of Fig. 2.

It is mentioned that in the low magnetic field, the effect of correlations increases the dielectric constant ε_o which increases the density of states at the Fermi level and decreases T_o [11]. However, as the magnetic field is increased, the correlation effect is reduced and T_o increases. In the literature, different expressions for the field dependence of T_o are proposed but only for the high field region where the shrinkage of the wave functions becomes important and the magnetoresistance is completely positive, that is, it is not affected by the negative component. In this regime, according to Shklovskii and Efros [8], T_o is expected to vary with B through the relation $T_o(B) \propto B/a(B)$, where $a(B)$ is the effective Bohr radius at a given field. This is expressed as:

$$a(B) = \hbar/\big(2m_e^* E_d(B)\big)^{1/2} \tag{2}$$

where m_e^* is the effective mass of the electron and $E_d(B)$ is the ionization energy at field B.

Thus, the increase in T_o with the field can be explained by the increase in $E_d(B)$ and thereby the decrease in $a(B)$. In a recent work [15], in the same sample CIS1, we have shown, from the analysis of the temperature and magnetic field dependence up to 35 T of the Hall coefficient data, that E_d remains practically constant at low fields and increases as $B^{1/3}$ at higher fields above around 8 T.

In the case of a sufficiently weak field defined by $\lambda \gg a$, where a is the state radius in zero field and $\lambda = (c\hbar/eB)^{1/2}$ is the magnetic length, the magnetic potential, which is proportional to λ^{-4}, is small compared to the Coulomb term $-e^2/\varepsilon_o r$ at distances of the order of a. Hence, for low field ($\lambda \gg a$), the electron wave function should not be affected and as reported in Ref. [15], the ground state ionization energy $E_d(B)$ should remain the same as $E_d(0)$ in zero field.

In the high field regime where $\lambda \ll a$, the magnetic field localizes an electron in a much narrower region than does the Coulomb potential. Hasegawa and Howard [16] proposed to express the wave function $\psi(r,z)$ in the form $\psi_o(r)F(z)$, where $\psi_o(r) = \frac{1}{\lambda\sqrt{2\pi}}\exp(-\frac{r^2}{4\lambda^2})$. The corresponding expression for the ionization energy is given by

$$E_d(B) = E_d(0)\big[\ln(a/\lambda)^2\big]^2 \tag{3}$$

This increases with B, but only for fields greater than the field B_o where $B_o = cm_e^{*2}e^3/\varepsilon_o^2\hbar^3$, is obtained from the condition $\lambda = a$. In the case of n-$CuInSe_2$, with $m_e^* = 0.09m_e$ and $\varepsilon_o = 9.3$, B_o is calculated to be 22 T. The increase in E_d with B corresponds to the condition $\ln(a/\lambda)^2 > 1$ and thereby $B > 2.7B_o$. This condition leads to $B > 60$ T for n-$CuInSe_2$. Since our measurements are only up to 35 T, this requirement is not satisfied in our case.

Table 2
Values of the two principal electronic orbital radii with the corresponding calculated values of T_o for the representative fields of 20, 25, 30 and 35 T

B (T)	20	25	30	35
$a_\perp$ (Å)	23.91	21.42	18.43	16.44
$a_\parallel$ (Å)	34.37	32.38	30.89	29.39
T_o (K)	31 396	41 523	58 796	77 662

Tokumoto et al. [11], using the percolation model, have proposed another relation for the localization temperature. This is expressed as

$$k_B T_o(B) = 0.372\big[N(E_F)a_\perp^2 a_\parallel\big]^{-1} \tag{4}$$

where $a_\perp$ and $a_\parallel$ are the two principal electronic orbital radii in the presence of the magnetic field. To calculate the field dependence of T_o, the values of $N(E_F), a_\perp$ and $a_\parallel$ are needed. By assuming a constant density of states for the impurity band and an energy spread comparable to the effective Rydberg, $N(E_F)$ for n-$CuInSe_2$ is estimated by employing the method used in the case of n-CdSe [17]. This is calculated to be 7.0×10^{18} eV^{-1} cm^{-3}. The values of $a_\perp$ and $a_\parallel$ for different values of B are obtained from the hydrogen-like impurity formalism used by Yafet, Keyes and Adams [18]. These values are shown in Table 2 together with the calculated values of T_o for some representative field values of 20, 25, 30 and 35 T. The values of T_o thus obtained by this method for different values of B are plotted in curve c of Fig. 2. Although the experimental and theoretical curves are very nearly parallel above 20 T, discrepancy of nearly one order of magnitude is noted. This could be related to the approximation used in the calculation of $N(E_F)$. A similar behavior has also been reported in InSb [19].

In conclusion, it is established that the electrical resistivity below 20 K in n-type $CuInSe_2$ at different field values up to 35 T follows Mott type variable range hopping conduction mechanism. The field dependence of the localization length ξ and the localization temperature T_o below 5 T can be explained as due to the presence of the negative magnetoresistance that is associated with the magnetic field induced delocalization effect. However, the observed decrease of T_o with increasing B above 10 T is in contradiction with the theoretical models. It is suggested that this behavior has its origin in the tendency of the magnetoresistance to saturate at higher field values. The expected variation of the localization temperature with the magnetic field is found when T_o is estimated from the linear extrapolation of the magnetoresistance above 10 T, in the region of saturation. The variation of T_o with B above 20 T shows the same tendency as predicted by the theory. However, smaller magnitude could be related to the estimated values of $N(E_F), a_\perp$ and $a_\parallel$ used in the calculation.

Acknowledgements

The experimental work was carried out by L. Essaleh as part of his doctoral program at the Laboratoire de Physique des Solides et Service National des Champs Magnétiques Pulsés of Toulouse. The growth of the samples, their characterizations and the detailed analysis of the magnetoresistance data were supported by grants from CONICIT (Contract No. G-97000670), CDCHT-ULA (Contracts Nos. C917-98-05A; C918-98-05-E), EEC (Contract No. CI1*-CT-92-0099VE) and the Franco Venezuelan Co-operation Program through CONICIT and CEFI.

References

[1] S.M. Wasim, Solar Cells 16 (1986) 289–316.
[2] M.A. Conteras, A.M. Gabor, A.L. Tennat, S. Asher, J.R. Tuttle, R. Noufi, Prog. Photovoltaics 2 (1994) 287–289.
[3] M.A. Conteras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Noufi, Prog. Photovolt: Res. Appl. 7 (1999) 311–313.
[4] L. Essaleh, J. Galibert, S.M. Wasim, E. Hernandez, J. Léotin, Phys. Rev. B 52 (1995) 7798–7801.
[5] L. Essaleh, J. Galibert, S.M. Wasim, J. Léotin, Phys. Stat. Sol. (b) 177 (1993) 449–457.
[6] L. Essaleh, S.M. Wasim, J. Galibert, J. Léotin, in: Proceedings of the 12 International Conference on Narrow Gap Semiconductors, Toulouse, 3–7 July, 2005, p. 234.
[7] L. Essaleh, J. Galibert, S.M. Wasim, E. Hernandez, J. Léotin, Phys. Rev. B 50 (1994) 18040–18045.
[8] B.I. Shkovskii, A.L. Efros, Electronic Properties of Doped Semiconductors, Springer, Berlin, 1984.
[9] L. Essaleh, S.M. Wasim, J. Galibert, J. Appl. Phys. 90 (2001) 3993–3997.
[10] O.V. Emel'yanenko, T.S. Lagunova, D.N. Nasledov, G.N. Talalkin, Sov. Phys. Solid State 7 (1965) 1063–1065.

[11] H. Tokumoto, R. Mansfield, M.J. Lea, Solid State Commun. 35 (1980) 961–964.
[12] N.V. Agrinskaya, V.I. Kozub, D.V. Shamshur, JETP 80 (1995) 1142–1146.
[13] K.G. Lisunov, E. Arushanov, G.A. Thomas, E. Bucher, J.H. Schön, J. Appl. Phys. 88 (2000) 4128–4134.
[14] R. Rosenbaum, T. Murphy, E. Palm, S. Hannahs, B. Brandth, Phys. Rev. B 63 (2001) 094426–094432.
[15] S.M. Wasim, L. Essaleh, C. Rincón, G. Marín, J. Galibert, J. Leotin, J. Phys. Chem. Solids 66 (2005) 1887–1890.
[16] H. Hasegawa, R.E. Howard, J. Phys. Chem. Solids 21 (1961) 179–198.
[17] A. Roy, M. Levy, X.M. Guo, P.M. Sarachik, Phys. Rev. B 39 (1989) 10185–10191.
[18] Y. Yafet, R.W. Keyes, E.N. Adams, J. Phys. Chem. Solids 1 (1956) 137–142.
[19] H. Tokumoto, R. Mansfield, M.J. Lea, Phil. Mag. B 46 (1982) 9–93.