



EFFECT OF THE STRONG MAGNETIC FIELD ON THE MOTT-VARIABLE RANGE HOPPING PARAMETERS IN *N*-TYPE COPPER INDIUM DISELENIDE

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We have measured the electrical resistivity ρ and the magnetoresistance in *n*-type CuInSe_2 samples with dopant concentration below the critical concentration for the metal insulator transition. Electrical conduction by variable range hopping (VRH) mechanism of Mott type is observed below 20 K in the same sample of *n*-type CuInSe_2 . The strong magnetic field dependence of the positive magnetoresistance, which shows a saturation behaviour, is analyzed with the existing theoretical models. Good agreement with the theory of the variation of the Mott VRH parameters T_0 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 $\ln \rho(B)/\rho(0)$ against $B^{1/3}$. This suggests that the departure of the hopping parameters 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.

Keywords: semiconductor, variable range hopping, magnetoresistance



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Introduction

The electrical conductivity of *n*-type CuInSe_2 (CIS), a promising material for opto-electronic and photovoltaic devices [1-3], down to liquid helium temperature in the variable range hopping (VRH) of Mott type and metallic conduction regimes are 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 quantum interference model, that explains the origin of NMR in very low fields, is 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 paper 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.

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 5N purity. 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].

Experimental results

The donor concentration N_D , the compensating acceptor concentration N_A and the activation energy E_D were calculated, using the approach of Emel'yanenko et al. [10] for the two bands model, from the temperature dependence of the Hall coefficient of CIS1 and CIS2 samples. These are, respectively, $6.82 \cdot 10^{16} \text{ cm}^{-3}$, $1.82 \cdot 10^{16} \text{ cm}^{-3}$ and 6.50 meV for CIS1, and $4.74 \cdot 10^{16} \text{ cm}^{-3}$, $7.40 \cdot 10^{15} \text{ cm}^{-3}$ and 8.64 meV for CIS2. With the dielectric constant $\epsilon_0 = 9.3$, the electron effective mass $m_e^* = 0.09 m_e$, the Bohr radius is calculated to be $a = 54.3 \text{ \AA}$. 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 $9.80 \cdot 10^{16} \text{ cm}^{-3}$. 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*-CuInSe₂ 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 $\rho = \rho_0 \exp[T_0(B)/T]^{1/4}$ 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_0 and the localization temperature T_0 , 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_0 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]

$$T_0 = \frac{\beta}{k_B N(E_F) \xi^3}, \quad (1)$$

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

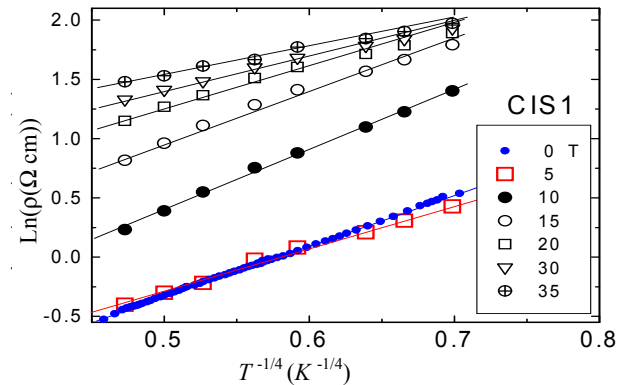


Fig. 1. The variation of the electrical resistivity ρ of a representative sample CIS1 as a function of temperature in the range 1.9 – 20 K at different fixed magnetic field values up to 35 T . The straight lines show the linear behavior

Table 1

Values of the parameters ρ_0 and T_0 in the Mott's law $\rho = \rho_0 \exp[T_0(B)/T]^{1/4}$ at different magnetic fields, obtained from a theoretical fit to the experimental data in the temperature range 4.2 – 20 K

$B(\text{T})$	0	1.5	5	8	10	15	20	30	35
$\rho_0 (\Omega \text{ cm}) (\cdot 10^{-4})$	866	925	1172	963	1000	2587	6062	12484	14044
$\Delta \rho_0 (\Omega \text{ cm}) (\cdot 10^{-4})$	70	10	70	63	100	300	700	1100	900
$T_0 (\text{K})$	324	278	187	557	813	440	147	39	7
$\Delta T_0 (\text{K})$	4	8	21	50	60	55	35	9	0.9

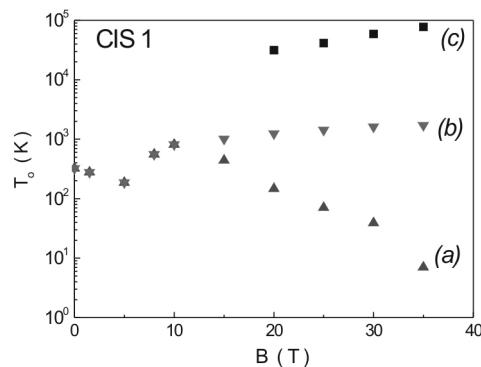


Fig. 2. The variation of the localization temperature T_0 as a function of magnetic field. The values T_0 obtained from the fit by the Mott's law $\rho \propto \exp[T_0/T]^{1/4}$ to the experimental data are shown in curve *a* and those obtained from extrapolation up to 35 T of $\text{Ln} \rho(B) \propto B^{1/3}$ data in curve *b*. The values of T_0 calculated with the method of Tokumoto et al. [11] are represented in curve *c*

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_0 , 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_0 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 reference [7]), T_0 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_0 . However, at higher field above 10 T , in range III, T_0 , 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_0 increases and tend to saturate at very high fields [11].

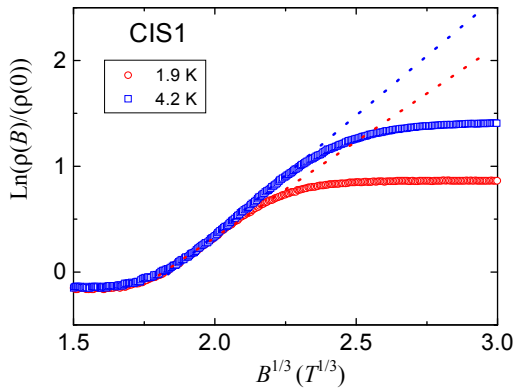


Fig. 3. A plot of $\ln[\rho(B)/\rho(0)]$ of a representative sample CIS1 as a function of $B^{1/3}$ at 1.9 and 4.2 K. The dotted lines show the linear behavior

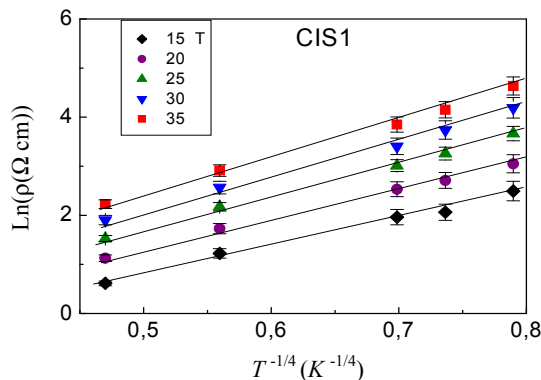


Fig. 4. The variation of $\ln \rho$ of a representative sample CIS1 as a function of $T^{-1/4}$ at different fixed magnetic fields. The data are obtained from extrapolating the $\ln \rho(B) \propto B^{1/3}$ curves up to 35 T. The straight lines show the linear behavior

The observed anomaly of T_0 , 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 lines. The values of $\ln \rho$, 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_0 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_0 which increases the density of states at the Fermi level and decreases T_0 [11]. However, as the magnetic field is increased, the correlation effect is reduced and T_0 increases. In the literature, different expressions for the field dependence of T_0 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_0 is expected to vary with B through the relation $T_0(B) \propto B/a(B)$, where $a(B)$ is the effective Bohr radius at a given field. This is expressed as:

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

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_0 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 $\lambda = (\hbar^2 / eB)^{1/2}$ is the magnetic length, the magnetic potential, which is proportional to λ^{-4} , is small compared to the Coulomb term $-e^2 / \epsilon_0 r$ 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 reference 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

$$\psi_0(r)F(z), \text{ where } \psi_0(r) = \frac{1}{\lambda\sqrt{2\pi}} \exp\left(-\frac{r^2}{4\lambda^2}\right).$$

The corresponding expression for the ionization energy is given by

$$E_d(B) = E_d(0) \left[\ln(a/\lambda)^2 \right]^2. \quad (3)$$

This increases with B but only for fields greater than the field B_0 where $B_0 = c m_e^* e^3 / \epsilon_0^2 \hbar^3$ is obtained from the condition $\lambda = a$. In the case of *n*-CuInSe₂, with $m_e^* = 0.09 m_e$ and $\epsilon_0 = 9.3$, B_0 is calculated to be 22 T. The increase in E_d with B corresponds to the condition $\ln(a/\lambda)^2 > 1$ and thereby $B > 2.7B_0$. This condition leads to $B > 60$ T for *n*-CuInSe₂. Since our measurements are only up to 35 T, this requirement is not satisfied in our case.

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

$$k_B T_0(B) = 0.372 [N(E_F) a_{\perp}^2 a_{\parallel}]^{-1}, \quad (4)$$

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_0 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*-CuInSe₂ is estimated by employing the method used in the case of *n*-CdSe [17]. This is calculated to be $7.0 \cdot 10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$. 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_0 for some representative field values of 20, 25, 30 and 35 T.

Table 2
Values of the two principal electronic orbital radii with the corresponding calculated values of T_0 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_0 (K)	31396	41523	58796	77662

The values of T_0 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 [18].

In conclusion, it is established that the electrical resistivity below 20 K in *n*-type CuInSe₂ 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_0 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_0 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_0 is estimated from the linear extrapolation of the magnetoresistance above 10 T, in the region of saturation. The variation of T_0 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.

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