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Electronic properties of nondegenerate strongly doped compensated semiconductors

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A theory of the electronic properties of strongly doped compensated (SDC) semiconductors is developed for finite temperatures, and in particular for the case when the electron gas in the entire semiconductor volume may be regarded as nondegenerate. It is shown that in the nondegenerate case and in the impurity conductivity region the characteristic size of the electron "drops" in the fluctuation potential wells increases with the temperature T initially as $\sim T^{-\frac{1}{2}}$ and subsequently as $\sim T^{-\frac{1}{3}}$. The density of states $g(\epsilon)$ in the vicinity of the initial (prior to doping) bottom of the conduction band is found in an energy range of the order of the characteristic depth ζ_0 of the largest fluctuation potential wells that still remain unscreened at $T=0$. In this energy range, $g(\epsilon)\sim\epsilon^{-\frac{1}{2}}$ for the chosen shape of the potential wells. The position of the Fermi level, the mean energy, and the specific heat of the electron gas in SDC semiconductors are calculated as functions of temperature in the range $0\leq t\leq\zeta_0$, by using the obtained form of the density of states. Some arguments are presented regarding the temperature dependence of the electric conductivity of SDC semiconductors in the indicated temperature range.

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The study of the electric properties of strongly doped compensated (SDC) semiconductors has recently been the subject of a number of both theoretical and experimental papers (see, e.g., [1–11]). Interest in these materials is due, first, to the fact that they constitute apparently one of the simplest examples of disordered solids, the electronic structure of which has not yet been sufficiently well studied. Second, SDC semiconductors are of interest from the practical point of view, for example for the development of most sensitive detectors of infrared and submillimeter radiation.[9]

In the customarily accepted quite obvious model of an SDC semiconductor, say of n-type, it is assumed that the free electrons remaining as a result of incomplete compensation, and numbering nV ($n=N_d-N_a$ is the electron density averaged over the crystal volume V, while N_d and N_a are the donor and acceptor densities averaged over the volume V) fill the deepest regions of the potential relief of the bottom of the conduction band, produced by the fluctuating potential of the impurities. The concentration of the electrons in these so-called electron drops, n_d, under conditions of strong compensation, greatly exceed the average density n and can be of the order of the density of the doping impurity (for example, 10^{15}–10^{16} cm^{-3} for n-InSb[9]). Thus, at helium temperatures the electron gas in the drops in SDC semiconductors can be regarded as degenerate. This is precisely the assumption under which Shklovskiĭ and Éfros constructed a theory of SDC semiconductors.[6]

With increasing temperature, however, the assumption that the electron gas is degenerate in the drops can cease to be satisfied. Thus, for example, in n-InSb at $n\sim10^{15}$ cm^{-3} the degeneracy temperature amounts to approximately 30 °K. Thus, at temperatures on this order or higher the electron gas in the drops must apparently be regarded as degenerate. An appreciable number of the experimental data lie in this temperature region.[8,9]

In this paper we attempt to construct, using the theory of Shklovskiĭ and Éfros[6] as a model, a theory for several electronic properties of SDC semiconductors, when the electron gas in a semiconductor, including also the drops, can be regarded as nondegenerate. One of the most important parameters of the theory of Shklovskiĭ and Éfros[6] is the characteristic dimension of the electron drop $R_q=a/(Na^3)^{1/9}$ ($a=\hbar^2\varkappa/me^2$ is the Bohr radius, $\varkappa$ is the dielectric constant of the crystal, m and e are the respective mass and charge of the electron, $N\approx N_d, N_a$). This dimension is obtained from the condition that the number of the quantum states in the attracting fluctuation of the impurity concentration be equal to the excess charges in it.[6] Let us find this parameter formally by a somewhat different method.

Namely, if the electrons having a characteristic kinetic energy ε are to be retained by a fluctuation potential well with depth on the order of γ, it is necessary to have

$$\gamma \approx \varepsilon. \tag{1}$$

Substituting here for the case of a degenerate electron gas in the fluctuation potential well with dimension R, $\varepsilon \approx \varepsilon_F^{(d)} \approx \hbar^2 n_d^{2/3}/2m$ (ε_F and n_d are the Fermi energy and the electron density in the drop) and $\gamma = \gamma(R) \approx e^2(NR^3)^{1/2}/\varkappa R$, [6] and assuming n_d to be equal to the concentration of the excess charge $(NR^3)^{1/2}/R^3$ in this fluctuation, we obtain directly for the drop radius R the value $R = R_q$.

With increasing temperature, the electrons in the drop will tend to occupy higher and higher energy states. We consider the region of characteristic electron energies

$$\varepsilon_F^{(d)} < \varepsilon < \zeta_0 \approx \gamma(R_c) \approx e^2 N^{2/3}/\varkappa n^{1/3}, \tag{2}$$

where $R_c = N^{1/3}/n^{2/3}$ is the maximum possible dimension of the fluctuation potential well at $T = 0$ and is determined by the screening (larger potential wells are screened), while ζ_0 is the Fermi level reckoned from the average value of the fluctuating potential and approximately equal to the fluctuation depth of a well with dimension R_c. [6]

At $R < R_c$ the potential of the fluctuation well is weakly screened and it can be regarded, as before, as equal to $\gamma(R)$. Since $\gamma(R)$ increases with increasing radius R, it is clear from the considerations presented above that the dimension of the characteristic region occupied by the electrons in the fluctuation potential well will increase with temperature. Using (1), it is easy to estimate the dimension of the region in this well, which can be occupied by electrons with characteristic energy ε. Substituting $\gamma = \gamma(R)$ in (1), we obtain

$$R_\varepsilon = R_q(\varepsilon/\varepsilon_F^{(d)})^2. \tag{3}$$

Here $\varepsilon_F^{(d)} \approx \gamma(R_q) \approx e^2(Na^3)^{4/9}/\varkappa a$ is the Fermi energy of the electron gas in the drop at $T = 0$ °K. It is easily seen that this formula is valid in the entire indicated energy interval, in particular, $R(\varepsilon = \varepsilon_F^{(d)}) = R_q$ and $R(\varepsilon \approx \zeta_0) \approx R_c$.

If the average electron energy is $\bar{\varepsilon} \gg \varepsilon_F^{(d)}$, then the electron gas in the drop can be regarded as nondegenerate and we can put $\varepsilon \sim T$ (T is the temperature in energy units). We then have from (3) for the characteristic dimension of the electron drop at the temperature T

$$R_T = R_q(T/\varepsilon_F^{(d)})^2. \tag{4}$$

We see thus that in the temperature region

$$(e^2/\varkappa a)(Na^3)^{4/9} \equiv T_1 < T < T_2 \equiv e^2 N^{2/3}/\varkappa n^{1/3} \tag{5}$$

the characteristic dimension of the electron drops in the fluctuation potential wells increases in proportion to the square of the temperature. We note that in SDC semiconductors we have the ratio

$$T_1/T_2 \approx (n/N)^{2/3}(Na^3)^{4/9} \equiv \alpha^{4/9} \ll 1$$

(see [6]), i.e., the temperature interval (5) can be quite large.

It is also of interest to note that when the electron gas in the drops is not degenerate the dimension of the electron drop, both at $T = 0$ °K (degenerate electron gas in drops) and at temperatures in the interval (5), coincides exactly with the corresponding Debye radius. In the expression for the Debye radius, naturally, it is necessary here to substitute the average electron density in the drop, i.e., the ratio of the number of electrons in the drop whose characteristic volume $(NR_q^3)^{1/2}/R_q^3$ or $(NR_T^3)^{1/2}/R_T^3$ respectively for the degenerate and nondegenerate cases. This fact can be understood on the basis of a definite analogy with the Thomas–Fermi model for a multielectron atom, where the dimension of the localization region of the wave functions of the electrons is of the order of the corresponding screening radius of the nuclear potential.

We consider now the temperature region

$$T_2 < T < T_3, \tag{6}$$

where T_3 is the temperature at which the intrinsic average electron density in the semiconductor becomes comparable with the average density $n = N_d - N_a$, i.e., starting with which the semiconductor becomes intrinsic. In this temperature region, the Debye screening radius turns out to be larger than R_c, the screening becomes weak, and the greater part of the electrons is no longer contained by the potential wells. Accordingly, the maximum possible dimension of the not-yet-fully screened potential well turns out to be of the order of the Debye radius. In this case this dimension coincides with the dimension of the corresponding electron drop, and increases in proportion to $T^{1/2}$

$$R_T = R_c(T/\zeta_0)^{1/2}. \tag{7}$$

The depth of the potential well $\gamma(R_T)$ turns out in this case to be smaller than T, in agreement with the notion of weak screening of the potential in this temperature region.

Shklovskiĭ and Éfros have concluded that the conductivity of an SDC semiconductor has an activation-type temperature dependence. [6] The activation energy ε_1 constitutes here the difference between the percolation level [6] and the Fermi level at zero temperature. However, as seen from the foregoing, when the temperature is increased (for example in the interval (5)), the electron gas in the drops becomes nondegenerate, and the Fermi level begins to depend on the temperature, namely, it drops. This means that the activation energy will increase with temperature, or more accurately speaking, the dependence of the kinetic coefficients on the temperature will in general not be described by a pure exponential law. It is clear that in this temperature region the kinetic coefficients will be determined mainly by electrons with energy on the order of T. Thus, to

estimate the dependence of the activation energy on the temperature it is necessary to find the density of states in the energy region (2), and accordingly the temperature dependence of the Fermi level in the temperature interval (5).

For an estimate of the density of states in this energy interval, we note that the number of the fluctuation potential wells with dimension R_ε (3), filled at an average electron energy $T > \varepsilon$, is $n/(NR_\varepsilon^3)^{1/2}$. On the other hand, the number of quantum states in one such well in the energy interval from ε to $\varepsilon + d\varepsilon$ is $2R_\varepsilon^3 d^3p/2\pi\hbar)^3$. We therefore obtain for the density of states

$$g(\varepsilon) \approx (nR_\varepsilon^{3/2}/N^{1/2}) g_0(\varepsilon) \approx g_0(\zeta_0)(\varepsilon/\zeta_0)^{7/2}, \quad (8)$$
$$g_0(\varepsilon) = (2m)^{3/2}\varepsilon^{1/2}/2\pi^2\hbar^3,$$

where $g_0(\varepsilon)$ is the density of states in the homogeneous semiconductor, and ζ_0 is given by formula (2). The energy is reckoned here from a certain arbitrary zero, located approximately at a distance $\zeta_0 = \gamma(R_c)$ below the average value of the fluctuating potential, i.e., the former bottom of the conduction band.

It is curious to note that the density of states near the former bottom of the conduction band is $g(\zeta_0) \approx g_0(\zeta_0)$, i.e., the situation is the same as if the action of the impurity were to cause the bottom of the conduction band to drop by an amount $\sim \zeta_0$. It is also easy to show that the Fermi level in the drop, at absolute zero temperature, calculated with the aid of the density of states (8) is the same: $\varepsilon_F^{(d)} \approx \gamma(R_q) \approx e^2(Na^3)^{4/9}/\varkappa a$,[6] thus indicating definitely that formula (8) is valid in the entire energy interval from 0 to ζ_0.

In principle, an exponential factor of the type $\exp[-(\varepsilon/\zeta_0)^2]$ can arise in the expression for the density of states (see, e.g.,[1-5]), and reflects the presence of fluctuation of various dimensions with corresponding statistical weights. This factor is missing from formula (8), since our entire analysis pertains to the energy interval $|\varepsilon| < \zeta_0$, and to a certain most probable average dimension of the fluctuations.

At energies $\varepsilon \gg \zeta_0$, the electrons can obviously be regarded as practically free and we can put $g(\varepsilon) \approx g_0(\varepsilon) \sim \varepsilon^{1/2}$. Thus, in the temperature interval $T \gg T_2 \approx \zeta_0$ we can use for the density of states, with good accuracy, the expression $g_0(\varepsilon) = (2m)^{3/2}\varepsilon^{1/2}/2\pi^2\hbar^3$. At temperatures $T \approx T_2$, on the other hand, the energy dependence of the density of states is apparently given by some law intermediate between $\varepsilon^{7/2}$ and $\varepsilon^{1/2}$. Using formula (8), we obtain the average electron energy ε and the dependence of the Fermi level of the electron gas on the temperature. We note that when finding the equilibrium characteristics of the system, such as the average energy or the Fermi level, the presence of exponentially damped tails in the density of states,[1-5] not accounted for by formula (8), will apparently not change strongly the result, inasmuch as in these tails there are few electrons.

In the temperature region $T \ll T_1 = \varepsilon_F^{(d)}$, the electron gas in the drops is degenerate. Calculating $\bar{\varepsilon}$ and the corrections to the Fermi level in the usual manner, we obtain

$$\bar{\varepsilon} \approx \frac{9}{11}\varepsilon_F^{(d)}\left[1 + \frac{11}{12}\pi^2\left(\frac{T}{\varepsilon_F^{(d)}}\right)^2\right], \quad (9)$$

$$\zeta(T) \approx \varepsilon_F^{(d)}\left[1 - \frac{7}{12}\pi^2\left(\frac{T}{\varepsilon_F^{(d)}}\right)^2\right], \quad (10)$$

where $\zeta(T)$ is reckoned from the same zero as in formula (8).

In the temperature interval $T_1 < T < T_2$ (5), assuming the electron gas to be nondegenerate, i.e., putting $\exp[\zeta(T)/T] \ll 1$, we obtain

$$\bar{\varepsilon} = {}^3/_2 T, \quad (11)$$
$$\zeta(T) = -{}^3/_2 T \ln(T/\varepsilon_F^{(d)}) - T \ln[{}^3/_2\Gamma({}^3/_2)]. \quad (12)$$

Knowing the expression for the density of states (8) and the position of the Fermi level (9), (10) in the temperature interval from 0 to T_2, we can obtain the different statistical characteristics of the electron gas in a SDC semiconductor. For example, for the specific heat of the electron gas $c_V = n\partial\bar{\varepsilon}/\partial T$ we obtain

$$c_V \approx {}^3/_2\pi^2 kn(kT/\varepsilon_F^{(k)}), \quad T < T_1, \quad (13)$$
$$c_V \approx {}^9/_2 kn, \quad T_1 < T < T_2 \quad (14)$$

(k is the Boltzmann constant). The average electron energy at the temperature T and the specific heat of the electron gas in the SDC semiconductor turn out to be larger than the corresponding values for the free electron gas with the same average concentration n. The reason is that when the temperature is increased an ever increasing part of the crystal volume becomes accessible to the electrons, i.e., the phase space in which the electrons are situated increases both on account of the momentum space (as in a homogeneous semiconductor) and on account of the coordinate space.

Using (8)–(10) for the number of electrons above the percolation level, i.e., the electrons that take part in the dc conductivity,[6] we obtain

$$n_p \approx [n/\Gamma({}^9/_2)](\zeta_0/T)^{7/2}\exp(-\zeta_0/T). \quad (15)$$

The corresponding dc conductivity $\sigma(T)$ of an SDC semiconductor is given by

$$\sigma(T) \approx e\mu(T)n_p(T)A(T), \quad (16)$$

where $\mu(T)$ is the electron mobility and $A(T)$ is a dimensionless factor that takes into account the change in the shape of the conducting channels between the electron drops and the temperature. Using for $A(T)$, for example, the expression obtained by Shik,[11] $A(T) \sim (T/\zeta_0)^{1/2}$, and putting $\mu(T) \sim T^\nu$, we obtain

$$\sigma(T) \sim T^{\nu+1/2}\exp(-\zeta_0/T), \quad T < T_1 \quad (17)$$

and

$$\sigma(T) \sim T^{\nu-3}\exp(-\zeta_0/T), \quad T_1 < T < T_2. \quad (18)$$

We can consider analogously also other electronic equilibrium and kinetic characteristics of an SDC semiconductor—the magnetic susceptibility, the light or sound

absorption coefficients, etc.

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Effect of high pressure and doping on the Curie temperature in chromium telluride

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Results of an experimental investigation of the effect of hydrostatic pressure (up to 12 kbar) on the Curie temperature T_c of solid $CrT_{1-x}X_x$ solutions (X = Se, Sb) are presented for concentration values x up to 0.5. The baric coefficients $\gamma = T_c^{-1}(dT_c/dP)$ of all alloys investigated are negative. However the form of $\gamma(x)$ is determined by the doping element X and accordingly by the nature of the compression, which can be either isotropic (X = Se) or anisotropic (X = Sb). Possible mechanisms of exchange spin coupling in the investigated alloys are discussed on the basis of the obtained data. It is concluded that two types of exchange interactions coexist in chromium telluride: 1) indirect exchange of localized electrons via the anion and 2) interaction between collectivized electrons in the narrow $3d$ band, and the energy of this interaction determines the Curie temperature.

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INTRODUCTION

The Curie temperature of chromium telluride depends very strongly on the variation of the interatomic distances, a fact resulting apparently from singularities in the exchange spin coupling in chalcogenides of $3d$ transition metals, the nature of which is not clear to this day. These questions have been intensively investigated in recent years both experimentally (see, e.g., [1,2]) and theoretically. [3,4]

In earlier studies[5,6] of chromium telluride at high pressures, attempts were made to distinguish between the influences exerted on the Curie temperature by two factors—volume changes and substitution of one anion for another by formation of solid solutions $CrTe_{1-x}X_x$, where X = S, Se, or Sb. It was established there that the Curie point T_c decreases with decreasing interatomic distance and the value of the derivative $dT_c/dV = 3 \cdot 10^{25}$ deg/cm^3 does not depend on the manner in which the lattice has been compressed, by hydrostatic pressure or by introducing the impurity S, Se, or Sb. The present paper is a continuation of the aforementioned research.

To answer the question why the Curie temperature of chromium telluride changes under hydrostatic compression and what is the mechanism that produces the exchange interactions in this alloy, we investigated two systems of solid solutions, $CrTe_{1-x}Se_x$ and $CrTe_{1-x}Sb_x$, which differ from each other in that when the tellurium atoms are replaced by selenium the hexagonal lattice becomes almost isotropically compressed (the alloys $CrTe_{1-x}Se_x$), and when the solid solutions $CrTe_{1-x}Sb_x$ are produced, an anisotropic change in volume takes place as a result of the strong decrease ot the hexagonal axis.

We present in this paper the results of an experimental investigation of the magnetization, the crystal-lattice parameters, and the baric characteristics of the Curie temperature (dT_c/dP and $\gamma = T_c^{-1}(dT_c/dP)$) of the alloys $CrTe_{1-x}Se_x$ and $CrTe_{1-x}Sb_x$ in the concentration interval $0 \leq x \leq 0.5$. On the basis of the obtained data we discuss the previously proposed mechanisms of the exchange interactions in chromium tellurides[1,4] and conclude that the observed regularities in the variation of the Curie temperature with pressure can be explained on the basis of the ferromagnetism of the collectivized electrons.