Anomalous Impurity Conductivity in n-GaSe and n-GaS (*) (**).

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Summary. — Evidence is reported for hopping conduction along the layers in n-GaSe and n-GaS. The results are compatible with the theoretical formulation given by Shklovskii for lightly doped semiconductors. The a.c. conductivity around and below room temperature follows the theoretical formula of Pollak and Geballe up to frequencies of 10^5 Hz. The anomaly lies in the fact that, with respect to previous measurements made on Si, Ge and InSb, the involved activation energies are much larger and the temperature at which the phenomenon takes place is much higher. At the present stage, hopping conductivity seems to be a peculiarity of n-type layer compounds. It seems to be indipendent of the direction of motion of carriers and somehow correlated to anion vacancies, which are likely responsible for the n-type conductivity of these compounds.

1. – Introduction.

The electrical properties of n-GaS [1] and n-GaSe, at temperatures below about 250 K, suggest the presence of an impurity or hopping conduction along the layers, even if partially anomalous in nature. Impurity conduction has been reported so far only at very low temperatures [2] for materials like Si,

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(1) C. MANFREDOTTI, R. MURRI, A. RIZZO and L. VASANELLI: *Sol. State Comm.*, **19**, 339 (1976).
(2) H. FRITSCHE and M. CUEVAS: *Phys. Lett.*, **119**, 1238 (1960); N. F. MOTT and W. D. TWOSE: *Adv. Phys.*, **10**, 107 (1961).

Ge or InSb, while, in the present case, hopping conduction starts just below room temperature, and it is characterized by relatively large ionization energies of the involved donors. We shall prove that the observed effects can be interpreted according to the theory developed by SHKLOVSKII [3] for cases of light doping and relatively strong compensation. Moreover, hopping conduction will also be evidenced for a.c. conduction, by proving that it obeys the well-known formula of Pollak-Geballe [4].

2. – Experimental and results.

The samples of GaSe were obtained by the iodine-assisted chemical transport method [5]; the GaS samples were cleaved from Bridgman ingots grown

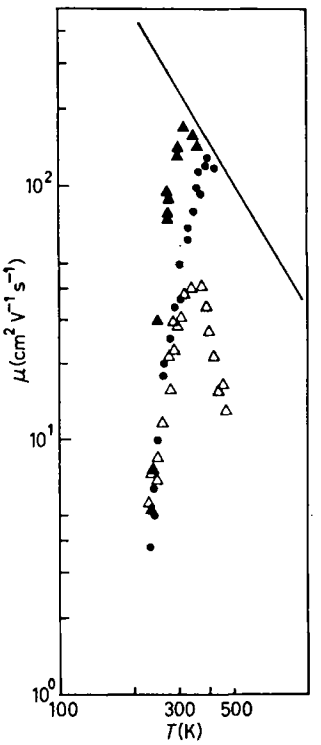

Fig. 1. – Behaviour of the electron mobility below room temperature in two samples of *n*-GaSe and in a sample of *n*-GaS. The behaviour of lattice mobility above room temperature is also indicated (solid line). GaSe: I_2, ▲ F44, • F49; △ GaS, BM12.

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[3] B. I. SHKLOWSKII: *Sov. Phys. Semicond.*, **6**, 1053 (1973).

[4] M. POLLAK and T. H. GEBALLE: *Phys. Rev.*, **122**, 1742 (1961).

[5] W. L. CARDETTA, A. M. MANCINI, C. MANFREDOTTI and A. RIZZO: *Journ. Crist. Growth*, **17**, 155 (1972).

with no intentional doping ([6]). All the samples were n-type, with a resistivity along the layers of about $10^7\,\Omega$ cm and a Hall mobility ranging between 40 and 150 $cm^2\,V^{-1}\,s^{-1}$ at room temperature for GaSe, and approximately the same resistivity and a Hall mobility ranging between 15 and 40 $cm^2\,V^{-1}\,s^{-1}$ for GaS. Typical sample dimensions were $(1\times1\times0.002)$ cm^3. The contact preparation and the experimental set-up have been previously described in detail ([1]). The measurements were carried out with the current flowing along the layers and the magnetic-field intensity for Hall measurements was 18 kG.

In fig. 1, both for Gas and GaSe, an abrupt decrease of the Hall mobility around room temperature can be observed. Obviously, scattering from charged impurities cannot be responsible for this effect; on the other hand, the impos-

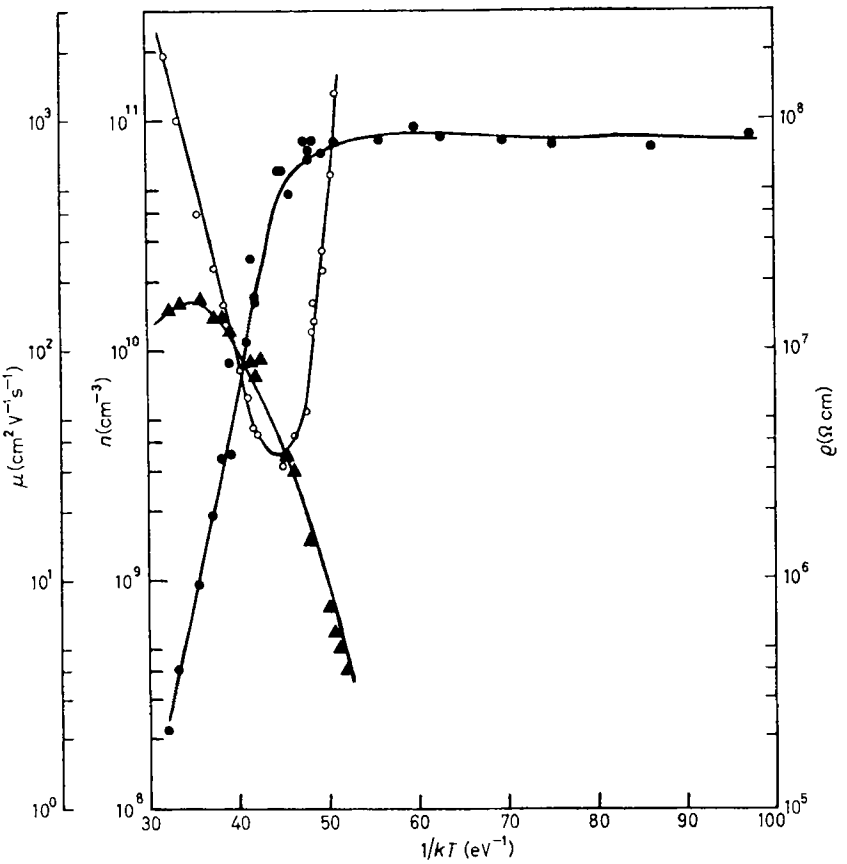

Fig. 2. – Behaviour of resistivity (ϱ), Hall mobility (μ) and electron concentration (n) as a function of temperature in a sample of n-GaSe. GaSe F44, • ϱ, ○ n, ▲ μ.

([6]) C. MANFREDOTTI, A. RIZZO, A. BUFO and V. L. CARDETTA: *Phys. Stat. Sol.*, **30** (a), 375 (1975).

sibility to detect any Hall mobility down 77 K helped to exclude the hypothesis of a change from n- to p-type conductivity.

TABLE I. – *Values of donor and acceptor concentrations* (N_D, N_A), *donors energies* (E_D), *Hall mobility activation energy* (E_H) *and compensation ratio* (K), *as derived by using the single-donor–single-acceptor model and eq.* (6).

Sample	N_D (cm^{-3})	N_A (cm^{-3})	$K = N_A/N_D$	E_D (eV)	E_H (eV)
GaSe F44	$2.08 \cdot 10^{16}$	$2.03 \cdot 10^{16}$	0.976	0.50	0.19
GaSe F49	$1.51 \cdot 10^{16}$	$1.49 \cdot 10^{16}$	0.987	0.50	0.15
GaS BM12	$6.40 \cdot 10^{16}$	$5.10 \cdot 10^{16}$	0.800	0.52	0.15
GaS BM14	$1.60 \cdot 10^{17}$	$1.40 \cdot 10^{17}$	0.870	0.51	0.15

If we go in more details (fig. 2), a saturation of the resistivity can be observed, while the Hall mobility shows a behaviour characterized by an activation energy, E_H, typical for a hopping process. The E_H value is practically the same both for GaSe and GaS samples (table I).

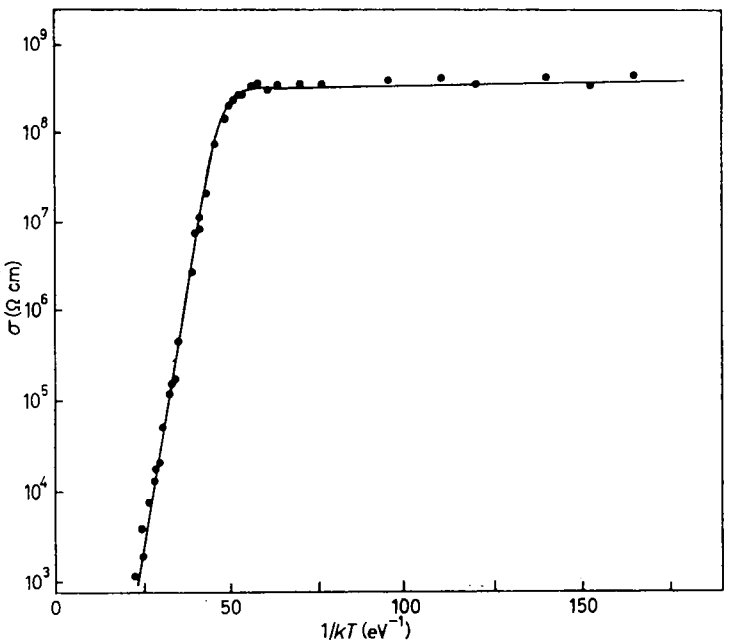

Fig. 3. – Fitting of a resitivity ϱ *vs.* the $(1/kT)$-curve for GaS, carried out by using eq. (1). The experimental errors are represented by the points themselves. BM12.

As is well known (7), the conductivity can be expressed in the whole temperature range in the form

$$\sigma = \sigma_1 \exp[-\varepsilon_1/kT] + \sigma_3 \exp[-\varepsilon_3/kT], \tag{1}$$

where the second term represents the impurity conductivity and $\sigma_1 \gg \sigma_3$. ε_1 is the donor activation energy and ε_3 is the activation energy for the hopping conduction in the impurity band. Generally, ε_3 is one order of magnitude less than ε_1 and σ_3 depends strongly on donor concentration. At is shown in fig. 3 for a GaS sample, the resistivity *vs.* temperature curves can be well fitted (confidence level 70%) with the relationship (1), even if ε_3 is probably too low to be determined exactly. The obtained values of the parameters for two GaS and two GaSe samples are reported in table II.

It is also well known (7) that a.c. conductivity at low frequencies in the case of phonon-assisted hopping conduction follows the Pollak-Geballe formula (4), which can be expressed as

$$\sigma(\omega) = \tfrac{1}{8}\pi e^2 kT[N(E_F)]^2 \alpha^{-5} \omega[\ln(\nu_{ph}/\omega)]^4, \tag{2}$$

TABLE II. – *Values of the «band resistivity» ϱ_1, hopping resistivity ϱ_3 and of their respective activation energies ε_1 and ε_3.* The average «impurity» distance R_c and the average «impurity» radius a are calculated according to eqs. (6).

Sample	ϱ_1 (Ω cm)	ϱ_3 (Ω cm)	ε_1 (eV)	ε_3 (eV)	R_c (Å)	a (Å)
GaSe F44	$4 \cdot 10^{-2}$	$8.5 \cdot 10^{7}$	0.48	$3.0 \cdot 10^{-3}$	300	30
GaSe F49	$1.5 \cdot 10^{-2}$	$6.3 \cdot 10^{7}$	0.67	$3.2 \cdot 10^{-3}$	330	33
GaS BM12	$4 \cdot 10^{-3}$	$1.3 \cdot 10^{8}$	0.52	$1.3 \cdot 10^{-2}$	204	19
GaS BM14	$1 \cdot 10^{-2}$	$2.7 \cdot 10^{8}$	0.50	$2.3 \cdot 10^{-2}$	150	14

where ω is the frequency, $N(E_F)$ is the density of localized levels ($cm^{-3}\,eV^{-1}$) at the Fermi level, α is defined so that $\exp[-\alpha r]$ is the rate at which the wave function of the localized state falls off with the distance and ν_{ph} is the phonon frequency. Since, as in our case, ν_{ph} is generally of the order of 10^{12} Hz, it can be shown that, for ω around 10^4 Hz, $\sigma \propto \omega^{0.8}$. Figure 4 shows exactly this kind of behaviour for GaSe and GaS in the quoted range of frequencies.

(7) N. F. MOTT and E. A. DAVIS: *Electronic Processes in Noncrystalline Materials* (Oxford, 1971).

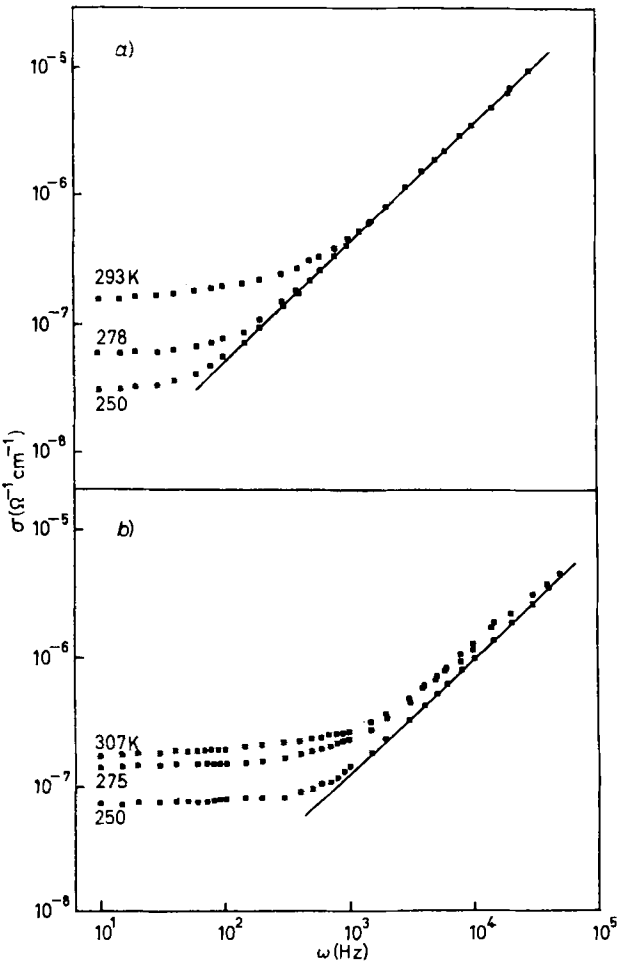

Fig. 4. – Behaviour of the a.c. conductivity $\sigma(\omega)$ as a function of the frequency for GaS and GaSe at various temperatures. Below $T = 250$ K, $\sigma(\omega)$ is independent of temperature in all the frequency range. *a*) GaS, BM12; *b*) GaSe: I_2, F49.

3. – Discussion.

Our data can be successfully analysed according to the theory of Shklovskii ([3]). This theory, under strong compensation condition ($N_D - N_A \ll N_D$), assumes the energy level scheme shown in fig. 12 of ref. ([3]). At low temperatures, the electrons occupy donors whose energies are considerably lowered by the potential energy of the neighbouring charged impurities. At moderately low temperatures, electrons can acquire energies at which density of states is high (isolated impurities). Such electrons can therefore jump between donors which are separated by distances of the order of $N_D^{-\frac{1}{3}}$. The assumptions of the

theory of Shklovskii can be summarized as follows:

$$N_D a^3 \ll 1 \qquad (a = \alpha^{-1}) \text{ light doping,} \tag{3}$$

$$\Delta\varepsilon = (N_D^{\frac{1}{3}} e^2)/x < \varepsilon_3 < e^2/xa = E\,. \tag{4}$$

By using the values reported in tables I and II, it is easy to verify that both conditions are fulfilled. Assuming as dielectric constants (along the layers) $x = 10.2$ for GaSe ([8]) and 7.5 for GaS ([9]), one obtains for the energy spread of the levels $\Delta\varepsilon$, 3.6 meV for GaSe and 9.2 meV for GaS, while for E one gets 0.44 eV and 1.1 eV, respectively. As one can note, condition (4) seems to be better verified for GaS than for GaSe. In conclusion, it seems well established that the theory of Shklovskii is valid also in a case in which deep levels are responsible for the impurity conduction.

Analysis of the data has been carried out in the following way: first of all, Hall data in the normal band conduction range have been analysed according to the well-known single-donor–single-acceptor model by using N_D, N_A and E_D as parameters ([1]). For m^*, the density-of-state effective mass, the values 1.3 m_e ([1]) and 1.0 m_e ([10]) have been used for GaS and GaSe, respectively. Now, since the method is not particularly sensitive to the value of N_D, while it is sensitive to $N_D - N_A$, N_D has been redetermined by taking into account the formula given by Shklovskii ([3]):

$$\varepsilon_3 = \frac{e^2 N_D^{\frac{1}{3}}}{x(N_D - N_A)^{\frac{1}{3}}} \tag{5}$$

and by using the values of ε_3 reported in table II.

Afterwards, the values of R_c, the average distance between donors, and the values of a ($= \alpha^{-1}$, the average radius of a level) have been calculated according to the equations

$$R_c = 0.82 N_D^{-\frac{1}{3}}, \qquad \varrho_3 = \varrho_1 \exp\,[1.8/N_D^{\frac{1}{3}} a] \tag{6}$$

and are reported in table II. The agreement can be considered good, we take into account that the theory is sensitive only to R_c/α, which is roughly 10 in all cases.

([8]) P. C. LEUNG, G. ANDERMANN, W. G. SPITZER and C. A. MEAD: *Journ. Phys. Chem. Sol.*, **27**, 849 (1966).

([9]) The values of the dielectric constant normally to c-axis, $\varepsilon_\perp$, has been obtained from the value of $\varepsilon_\parallel$ (C. H. SEQUINand M-A. NICOLET: *Sol. Stat. Electron.*, **14**, 421 (1971)), by assuming the same $\varepsilon_\perp/\varepsilon_\parallel$ ratio of the GaSe.

([10]) C. MANFREDOTTI, A. MANCINI, R. MURRI, A. RIZZO and L. VASANELLI: submitted for pubblication to *Nuovo Cimento*.

A numerical analysis has been carried out also for the results of $\sigma(\omega)$ measurements. By using eq. (3), which has been multiplied by E_F/kT [7], since $\sigma(\omega)$ is apparently independent of T (fig. 4), values of $N(E_F) = 8 \cdot 10^{17}$ cm^{-3} (eV)$^{-1}$ for GaSe and $4.5 \cdot 10^{18}$ cm^{-3} (eV)$^{-1}$ for GaS have been obtained. These values are not unreasonable, since they should be certainly lower than $N_D/\Delta\varepsilon$, which is $5 \cdot 10^{18}$ cm^{-3} (eV)$^{-1}$ for GaSe and $1.2 \cdot 10^{19}$ cm^{-3} (eV)$^{-1}$ for GaS, by using eq. (5) for $\Delta\varepsilon$.

The complete comparison between values of ω_0, τ^{-1} and σ_3 obtained from the experimental results of $\sigma(\omega)$ and the theoretical ones according to the Pollak-Geballe theory are reported in table III. In this table ω_0 is the frequency at

TABLE III. – *Values of experimentally determined and theoretically calculated values of the frequency ω_0, of the reciprocal of the mean time for phonon-assisted tunnelling (τ^{-1}) and for the* d.c. *conductivity, due to electrons with energy near E_F, (σ_3).* For the calculations, see the text.

Sample	ω_0 (s^{-1}) (experimental)	ω_0 (s^{-1}) (theoretical)	τ^{-1} (s^{-1}) (experimental)	τ^{-1} (s^{-1}) (theoretical)	σ_3 (Ω^{-1} cm^{-1}) (experimental)	σ_3 (Ω^{-1} cm^{-1}) (theoretical)
GaSe	$6 \cdot 10^2$	$1.4 \cdot 10^2$	$6.8 \cdot 10^3$	$7.9 \cdot 10^3$	$1.3 \cdot 10^{-8}$	$1 \cdot 10^{-8}$
GaS	$5.8 \cdot 10$	$5.8 \cdot 10$	$1.9 \cdot 10^3$	$1.7 \cdot 10^3$	$5 \cdot 10^{-9}$	$3.8 \cdot 10^{-9}$

which the $\omega^{0.8}$ behaviour takes over from the d.c. process, τ is the mean time for phonon-assisted tunnelling and $\sigma_3 = \varrho_3^{-1}$ is the d.c. conductivity due to hopping by electrons with energies near E_F (eq. (2) and table II). Experimentally, τ^{-1} has been determined as the average frequency in the $\omega^{0.8}$ region. Theoretically, it is given by the relationship

$$\tau^{-1} = \nu_{ph} \exp[-2\alpha R]. \tag{7}$$

ω_0 is the frequency at which $\sigma(\omega) = \sigma(0)$. For $\sigma(\omega)$, use has been made of eq. (3), with the reported values of $N(E_F)$, α^{-1}, while ν_{ph} has been calculated by using phonon energies $\hbar\omega = 16.7$ meV for GaSe and 22 meV for Gas [11]. For $\sigma(0)$ the following relationship has been used [7]:

$$\sigma(0) = (\sigma_3)_{th} \exp[-\varepsilon_3/kT], \tag{8}$$

where

$$(\sigma_3)_{th} = e^2 R^2 \nu_{ph} N(E_F) \exp[-2\alpha R]. \tag{9}$$

The overall agreement is clearly satisfactory and further supports the evidence of a hopping mechanism both in GaS and in GaSe.

[11] PH. SCHMID: Thesis, Lausanne (1974).

4. – Conclusions.

The comparison with existing theories strongly supports the fact that impurity conduction takes place in n-GaS and n-GaSe. The observed phenomenon represents one of the few cases observed in highly compensated semiconductors, and certainly the first one in which the levels involved in hopping conduction are deep and, consequently, the phenomenon takes place at relatively high temperatures.

Taking into account previous measurements on other n-type layer semiconductors ([12]), it appears that hopping behaviour is simply due to the random distribution of impurities. The « impurities », in this case, should certainly be S vacancies in the case of GaS ([13]) and probably, if we take into account the similarity of results, Se vacancies for GaSe. The values obtained for the average radii a of these defects seem quite reasonable, and together with the values of the average distance between the defects themselves R allow a reasonable comparison with the formulae for a.c. conductivity, which depend strongly both on a and on R.

These kind of defects seem to involve two layers in the case of GaS and four layers in the case of GaSe, even if most likely the corresponding wave functions are anisotropic and the quoted values of a are to be intended as averages also with respect to the various directions.

At the present stage, the impurity conduction seems a peculiarity of n-type layered semiconductors and to be somehow related to anion vacancies. It may also be that this kind of impurity conduction involves chains of defects extending along the layers, in the interlayer spacing.

([12]) J. P. GOWERS and P. A. LEE: *Sol. State Comm.*, **8**, 1447 (1970); S. M. ATAKISHEV and G. A. AKHUNDOV: *Phys. Stat. Sol.*, **32**, K33 (1969); R. H. TREDGOLD and A. CLARK: *Sol. State Comm.*, **7**, 1519 (1969).

([13]) R. M. A. LIETH and F. VAN MAESEN: *Phys. Stat. Sol.*, **10** (a), 73 (1072).

● RIASSUNTO (*)

Si fornisce la prova per la conduzione tipo hopping lungo gli strati nel n-GaS e n-GaSe. I risultati sono compatibili con la formulazione teorica data da Shklovskii per semiconduttori debolmente drogati. La conducibilità in c.a. al di sotto della temperatura ambiente segue la formula teorica di Pollak e Geballe fino a frequenze di 10^5 Hz. L'anomalia sta nel fatto che, rispetto a misure precedenti fatte su Si, Ge ed InSb, le energie di attivazione coinvolte sono molto più grandi e la temperatura alla quale il fenomeno accade è molto più alta. Allo stato attuale la conduttività tipo hopping sembra essere una peculiarità dei composti a strati del tipo n. Sembra anche che sia indipendente dalla direzione del moto dei portatori ed in qualche modo correlata alle vacanze anioniche che sono probabilmente responsabili per la conduttività n di questi composti.

(*) *Traduzione a cura della Redazione.*

Аномальная примесная проводимость в n-GaSe и n-GaS.

Резюме (*). — Приводится подтверждение «прыжковой» проводимости вдоль слоев в n-GaSe и n-GaS. Полученные результаты сходны с теоретической формулировкой, предложенной Шкловским для полупроводников с незначительными присадками. Проводимость переменного тока вблизи и ниже комнатной температуры подчиняется теоретической формуле Поллака и Джебалла вплоть до частот 10^5 гц. Аномалия заключается в том, что по сравнению с предыдущими измерениями на Si, Ge и InSb, рассматриваемые энергии активации оказываются много большими, а температура, при которой имеет место это явление, более высокой. В данном случае «прыжковая» проводимость характерна для слоистых соединений n-типа. Указанная проводимость не зависит от направления движения носителей и связана с анионными вакансиями, которые, вероятно, ответственны за проводимость n-типа этих соединений.

(*) *Переведено редакцией.*