ISSN 0021-3640, JETP Letters, 2012, Vol. 96, No. 3, pp. 184–187. © Pleiades Publishing, Inc., 2012.
Original Russian Text © N.V. Perunov, A.F. Shevchun, N.D. Kushch, M.R. Trunin, 2012, published in Pis'ma v Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki, 2012, Vol. 96, No. 3, pp. 197–200.

Surface Impedance of k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br Crystals

N. V. Perunov[a, b], **A. F. Shevchun**[a], **N. D. Kushch**[c], **and M. R. Trunin**[a, d]

[a] *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia*
[b] *Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
[c] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia*
[d] *Moscow Institute of Physics and Technology, Dolgoprudnyi, Moscow region, 141700 Russia*

Received May 22, 2012; in final form, July 5, 2012

Precision measurements of the real and imaginary parts of the microwave surface impedance $Z_{ac}(T) = R_{ac}(T) + iX_{ac}(T)$ of the conducting ac layers of the k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystals in the temperature interval of $0.5 < T < 100$ K have demonstrated a series of features: (i) the temperature course of the field penetration depth is close to linear $\Delta\lambda_{ac}(T)\propto\Delta X_{ac}(T)$ in the superconducting state at $T \ll T_c \approx 11.5$ K; (ii) the curves $R_{ac}(T) = X_{ac}(T)$ coincide at $T_c < T < 40$ K; (iii) the $X_{ac}(T)$ value at $T > 40$ K increases in comparison with $R_{ac}(T)$; (iv) the dependence $R_{ac}(T)$ at $T > 40$ K is nonmonotonic in thin crystals. These features of the impedance $Z_{ac}(T)$ with increasing T are interpreted in terms of (i) the d-type symmetry of the superconducting order parameter, (ii) normal skin effect, (iii) manifestations of the antiferromagnetic fluctuations, and (iv) the size effect. The electrodynamic parameters of k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br have been determined.

DOI: 10.1134/S0021364012150088

The problem of the type of superconducting interaction, symmetry of the order parameter, and features of the normal state of organic superconductors has been a subject of intense discussions until now.

Layered k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystals have orthorhombic symmetry and are built of conducting cation–radical ac layers of BEDT-TTF alternating with the dielectric layers of Cu[N(CN)$_2$]Br single-charge anions [1, 2]. In the k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br unit cell, there are four pairs (dimers) of donor BEDT-TTF molecules (two dimers in the conducting layer). Each dimer gives one conduction electron. The two-dimensional Fermi surface of k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br consists of closed quasi-two-dimensional hole orbits (α pockets) located on the two k_a edges of the Brillouin zone and open electron sheets crossing these edges in the k_c direction [2, 3]. The simplest estimates give the values of the carrier density $n \approx 10^{21}$ cm^{-3} and the Fermi energy $E_F \sim 1000$ K.

Superconducting k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystals at normal pressure have the maximum critical temperature of the superconducting transition ($T_c \approx 11.5$ K) for all known organic ion-radical salts and are strongly anisotropic: the ratio of the resistivities across (ρ_b) and along (ρ_{ac}) the ac layers reaches 10^4–10^5 at liquid helium temperatures [4]. Therefore, when $\rho_{ac}(T)$ is measured at direct current, even a slight misalignment of the contacts with respect to the crystal axes always leads to the "admixture" of the component proportional to $\rho_b(T)$ to the measured signal. Since $\rho_b(T) \gg \rho_{ac}(T)$ in k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, the ρ_{ac} value at a given temperature obtained at direct current exceeds the true ρ_{ac} value, and the temperature dependence $\rho_{ac}(T)$ reflects the main features of $\Delta\rho_b(T)$. Noncontact microwave measurements of anisotropic layered high-temperature superconductors [5] provide the high-frequency current flow strictly in the conducting layers so that the imperfections of the crystal surface and shape do not introduce distortions in the measured quantities. It is also essential that the microwave response characterizes both the normal and superconducting states of the studied material.

We present the first precision measurements of the surface impedance components in the ac planes of superconducting k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystals in the temperature interval $0.5 < T < 100$ K in the millimeter wavelength range. Two samples grown by the electrochemical oxidation method were studied [6]. They were of the shape of approximately rectangular thin plates with dimensions $a \times c \times b \approx 0.5 \times 0.5 \times 0.1$ mm and $0.55 \times 0.25 \times 0.03$ mm. The surface impedance $Z(T) = R(T) + iX(T)$ was measured by the hot finger method at the frequency $f = 28.2$ GHz [7]. In turn, the samples were set on the butt end of a sapphire rod so that the crystal b axis was directed along the microwave magnetic field. The high-frequency current flowed in the crystal ac planes as shown in the inset of Fig. 1b.

Figure 1 shows the temperature dependences of the surface impedance of crystals 1 and 2. The critical temperature of the superconducting transition for both crystals determined from the beginning of the

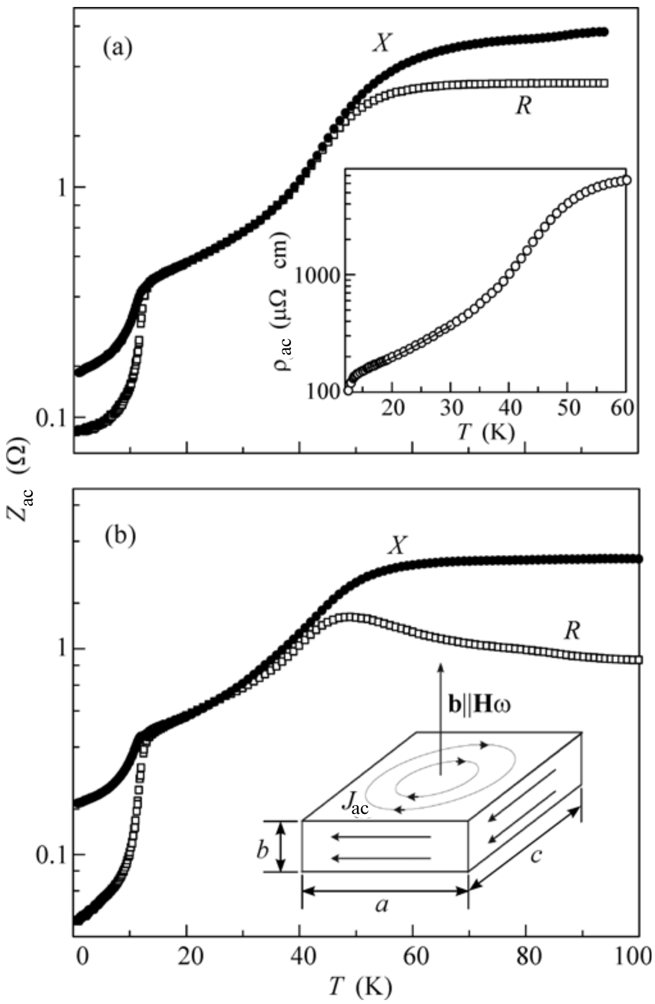

Fig. 1. Temperature dependences of the surface impedance $Z = R + iX$ in the conducting *ac* planes of crystals (a) 1 and (b) 2. Insets: (a) the dependence $\rho_{ac}(T) = 2R^2(T)/\omega\mu_0$ in sample 1 and (b) orientation of the crystals with respect to the microwave magnetic field in the resonator.

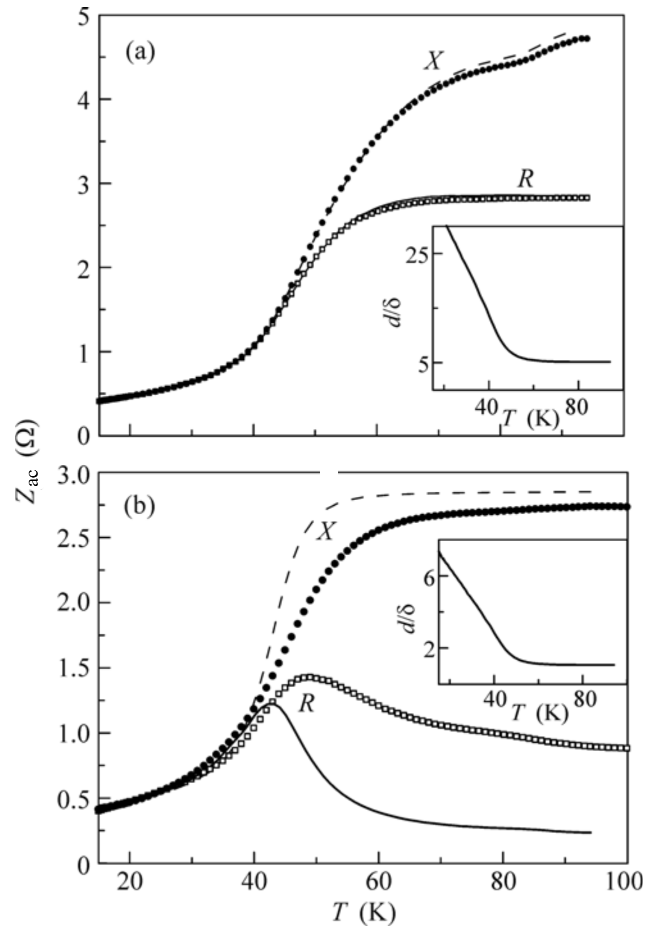

Fig. 2. Temperature dependences of the surface impedance components (curves) calculated taking into account the size effect and (points) measured in crystals (a) 1 and (b) 2. Insets show the temperature dependences of the ratio of the sample thickness d to the skin layer depth $\delta(T)$.

sharp drop of $X(T)$ is approximately the same ($T_c \approx$ 11.5 K). The characteristic width of the superconducting transition of the samples found from the measurements of the dynamic susceptibility at a frequency of 100 kHz was about 0.2 K.

At $T > T_c$, there is a small temperature interval ($15 \le T \le 45$ K for sample 1 in Fig. 1a and $15 \le T \le 30$ K for sample 2 in Fig. 1b) where the curves of the surface resistance $R(T)$ and reactance $X(T)$ can be superposed, $R(T) = X(T)$, which corresponds to the condition of the normal skin effect. The temperature dependence of the resistivity in the *ac* plane of sample 1 found from the formula $\rho_{ac}(T) = 2R^2(T)/\omega\mu_0$ is shown in the inset of Fig. 1a. It has the form $\rho_{ac}(T) \approx A + BT^3$ in the interval $15 \le T \le 30$ K corresponding to the Bloch–Grüneisen law with the Debye temperature $T_D \sim 150$ K. The resistivity $\rho_{ac}(15\text{ K}) \approx 150$ μΩ cm is much higher than the typical resistivity of normal metals and at $T \approx 40$ K it reaches the limiting Ioffe–Regel value (~1 mΩ) [8], tending to saturation with increasing temperature. Indeed, determining the scattering time $\tau(T_c) \approx 5 \times 10^{-13}$ s from our measurements of impedance [9] and using the estimate of the Fermi velocity $v_F \approx 6 \times 10^6$ cm/s in *k*-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br from [3], we find that the mean free path $l_{ac} \approx 1$ nm at $T \approx 50$ K is comparable with the size of the unit cell in the *ac* plane.

The $\rho_{ac}(T_c)$ value in our crystals is an order of magnitude less than the $\rho_{ac}(T_c)$ values found from the dc measurements of *k*-Br [10]. In addition, $\Delta\rho_{ac}(T) \propto T^3$ in the region of the normal skin effect in Fig. 1a, while $\Delta\rho_{ac}(T) \propto T^2$ in [10] (quadratic temperature dependence is characteristic of the increase in resistivity $\Delta\rho_b(T) \propto T^2$ at $T_c < T < 40$ K). These differences are due to the contribution of the transverse component

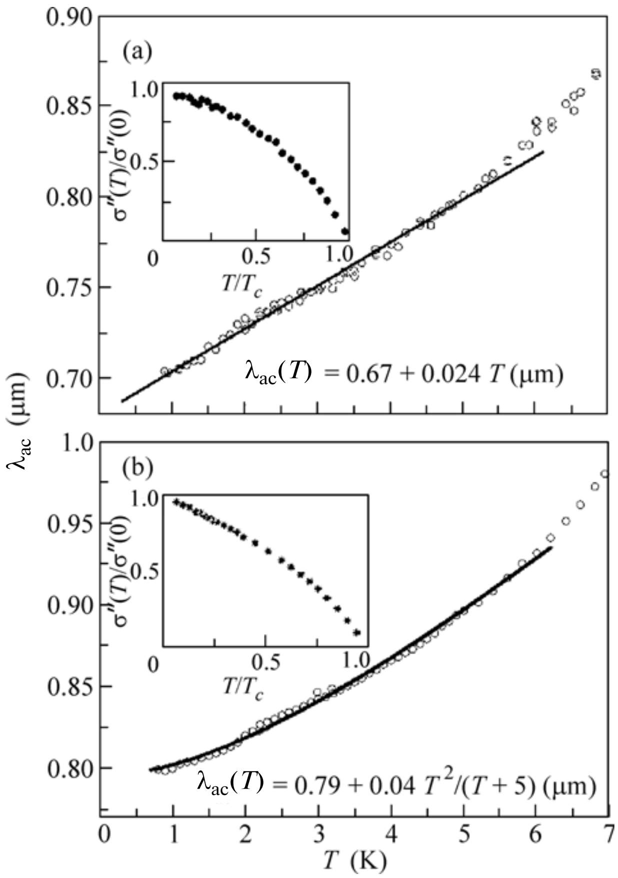

Fig. 3. Measured temperature dependences of (open circles) the field penetration depth and imaginary parts of (closed circles in the insets) conductivity in samples (a) 1 and (b) 2. Solid lines and formulas in the bottom parts of the figure are the results of least-squares fitting of the experimental data $\lambda_{ac}(T)$ in the interval $0.5 \le T \le 6$ K to the dependence $\lambda_{ac}(T) = \lambda_{ac}(0) + bT^2/(T + T^*)$ [18].

$\rho_b(T)$ of the resistivity to the direct-current measurements of $\rho_{ac}(T)$.

According to the phase diagram, the state of k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br at $T > 40$ K is called bad metal [11]. In this state, in addition to the saturation of the resistivity $\rho_{ac}(T)$, temperature anomalies are distinctly observed in the magnetic susceptibility [12], ultrasound propagation velocities [13], and nuclear spin relaxation [14]. These anomalies are interpreted in terms of the transition from the Fermi liquid behavior at low temperatures to the antiferromagnetic fluctuation mode [11]. In our measurements, the considerable excess of the $X(T)$ value over $R(T)$ at $T > 40$ K in both samples is obviously atypical for bad metals (Fig. 1). It is well known that, e.g., the measured reactance $X(T)$ of the conducting layers in the normal state of high-temperature superconductors is somewhat less than their surface resistance $R(T)$. However, taking into account the positive thermal expansion of crystals leads to the increase in $X(T)$ to $R(T)$ [5]. As a result, at $T > 100$ K, the normal skin effect takes place in the high-temperature superconductors: $X(T) = R(T)$. The features of the thermal expansion of k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [15] hardly affect the measured curves $X(T)$ at $T > 40$ K. However, the magnetic contribution to $X(T)$ may be provided by the nonzero imaginary component μ'' of the dynamic magnetic permeability $\mu = 1 + i\mu''$ [16], which is responsible for the energy absorption by the magnetic system. Taking into account the dependence $\mu''(T)$ when finding the real and imaginary parts of the impedance in the local approximation $Z = R + iX = (i\mu_0\mu\omega/\sigma)^{1/2}$ may lead to the increase in $X(T) > R(T)$ observed in Fig. 1.

Another feature of the temperature dependences of impedance in Fig. 1 is the different behaviors of the curves $R(T)$ at $T > 40$ in samples 1 and 2: $R(T)$ in sample 2 reaches the maximum at $T \approx 50$ K and then decreases with increasing temperature. Such a behavior is caused by the manifestation of the size effect in sample 2, the thickness $d \approx 30$ μm of which is comparable with the field penetration depth $\delta(T)$ in the sample. At $T \approx T_c$, the skin layer depth is $\delta = (2\rho/\omega\mu_0)^{1/2} \approx 10$ μm. It can be seen in the inset of Fig. 2b that $d/\delta(50\text{ K}) \approx 1$ at temperatures of about 50 K. Therefore, the $R(T)$ and $X(T)$ values measured in sample 2 should be interpreted as the components of the effective (including the size features) impedance $Z_{\text{eff}}(T)$, which in the limiting case $\delta \ll d$ should coincide with the surface impedance $Z(T)$ of a semi-infinite plate.

The calculations show that the $Z(T)$ and $Z_{\text{eff}}(T)$ components in sample 1 ($d/\delta(T) \gg 1$) almost coincide over the entire temperature interval (Fig. 2a). Thus, the $R(T)$ and $X(T)$ dependences measured in sample 1 should be considered true ("semi-infinite") components of the surface impedance in the *ac* planes of the bulk k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystal. Figure 2b shows the results of the calculation of the effective impedance components in sample 2 (solid and dashed curves). For that the data for sample 1 were used as true $R(T)$ and $X(T)$ values. It is seen that the calculated curves for sample 2 coincide with those measured at $T < 40$ K in the region of the normal skin effect and qualitatively present the behavior at $40 < T < 100$ K in the region where the size effect in sample 2 becomes significant.

The measurements of the reactance $X(T)$ at $T < T_c$ make is possible to determine the temperature dependences of the field penetration depth in the conducting layers of superconductors 1 and 2: $\lambda(T) = X(T)/\omega\mu_0$ (Fig. 3). The k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystals in which the coherence length in the *ac* plane $\xi_0 \approx 4$ nm [17] are pure ($l(T_c) > \xi_0$) London ($\lambda > \xi_0$) superconductors. Therefore, the $\lambda_{ac}(T)$ values given in Fig. 3 correspond to the London depth $\lambda_L(T)$.

The $\lambda_{ac}(0.6\text{ K}) \approx \lambda_L(0) \approx 0.7$ μm values in samples 1 and 2 measured at the minimum temperature differ less than by 20%. The $\lambda_{ac}(T)$ curves in Fig. 3 are obviously and, therefore, the k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystals are not conventional Bardeen–Cooper–Schrieffer superconductors with the s-type symmetry of the order parameter. The $\lambda_{ac}(T)$ dependence for sample 1 agrees well with the linear dependence $\lambda_L(T) = \lambda_L(0) + \alpha T = 0.67 + 0.024T$ [μm] at $T < T_c/2$ (Fig. 3a), while the dependence for sample 2 is linear in the interval $2.5 < T < 6$ K but switches to quadratic at $T < 2.5$ K. It was shown in [18] that such a behavior is inherent in superconductors with the d-type symmetry of the order parameter, in which the crossover from the linear to the quadratic temperature dependence of the field penetration depth ($T < T^* < T_c$) is due to the resonance scattering on impurities in the low-temperature region and is described to the interpolation formula $\lambda(T) - \lambda(0) = bT^2/(T + T^*)$. The parameters that provide the best fit of the data to this formula are given in Fig. 3 ($T^* \ll 0.5$ K in sample 1). The shape of the temperature dependences of the imaginary parts of the conductivity $\sigma''(T)/\sigma''(0) = \lambda^2(0)/\lambda^2(T)$ in the insets of Fig. 3 is similar to those observed in high-temperature superconducting crystals [5]. This also indicates the nontrivial symmetry of the superconducting order parameter in k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Similar results of the measurements of $\Delta\lambda_{ac}(T)$ and conclusions about the nature of the superconducting state in k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were presented earlier in [19, 20].

To conclude, the microwave measurements of the surface impedance components in the *ac* planes of the k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystals with $T_c \approx 11.5$ K demonstrate a series of features in the superconducting and normal states of these crystals. First, the measurements at $T \ll T_c$ indicate the d symmetry of the superconducting order parameter. Second, in the interval $T_c < T < 40$ K, the $R(T)$ and $X(T)$ curves coincide (the normal skin effect) and the temperature dependence of the resistivity is $\Delta\rho_{ac}(T) \propto T^3$. Finally, at $T > 40$ K, the resistance tends to saturation (the Ioffe–Regel limit) and the $X(T)$ value becomes larger than $R(T)$ owing to the additional contribution of the antiferromagnetic spin fluctuations. The $\lambda_L(0) \approx 0.7$ μm, $l(T_c) \approx 30$ nm, and $\delta(T_c) \approx 10$ μm values were determined.

We are grateful to V.N. Zverev, M.V. Kartsovnik, R.P. Shibaeva, and E.B. Yagubskii for useful discussions. This work was supported by the Russian Foundation for Basic Research (project nos. 11-02-12071-ofi-m and 12-02-01009-a), the Ministry of Education and Science of the Russian Federation (state contract no. 0911, federal program "Human Capital for Science and Education in Innovative Russia"), and the Russian Academy of Sciences (basic research programs).

REFERENCES

1. A. M. Kini, U. Geiser, H. H. Wang, et al., Inorg. Chem. **29**, 2555 (1990).
2. T. Ishiguro, K. Yamaji, and G. Saito, Springer Ser. Solid-State Sci. **88**, (1998).
3. H. Weiss, M. V. Kartsovnik, W. Biberacher, et al., Phys. Rev. B **59**, 12370 (1999).
4. J. Singleton and Ch. Mielke, Contemp. Phys. **43**, 63 (2002).
5. M. R. Trunin, Phys. Usp. **41**, 843 (1998); Phys. Usp. **48**, 979 (2005).
6. L. I. Buravov, N. D. Kushch, V. A. Merzhanov, et al., J. Phys. I France **2**, 1257 (1992).
7. A. F. Shevchun and M. R. Trunin, Instrum. Exp. Tech. **49**, 669 (2006).
8. O. Gunnarsson, M. Cakandra, and J. E. Han, Rev. Mod. Phys. **75**, 1085 (2003).
9. M. R. Trunin, Yu. A. Nefyodov, and H. J. Fink, J. Exp. Theor. Phys. **91**, 801 (2000).
10. S. Yasin, M. Dumm, B. Salameh, et al., Eur. Phys. J. B **79**, 383 (2011).
11. M. Dressel, J. Phys.: Condens. Matter **23**, 293201 (2011).
12. T. Sasaki, N. Yoneyama, A. Matsuyama, et al., Phys. Rev. B **65**, 060505 (2005).
13. K. Frikach, M. Poirier, M. Castonguay, and K. D. Truong, Phys. Rev. B **61**, R6491 (2000).
14. A. Kawamoto, M. Miyagawa, N. Nakazawa, et al., Phys. Rev. Lett. **74**, 3455 (1995).
15. J. Muller, M. Lang, F. Steglich, et al., Phys. Rev. B **65**, 144521 (2002).
16. D. P. Choudhury, H. Srikanth, S. Sridhar, and P. S. Canfield, Phys. Rev. B **58**, 14490 (1998).
17. W. K. Kwok, U. Welp, K. D. Karrlson, et al., Phys. Rev. B **42**, 8686 (1990).
18. P. J. Hirschfeld and N. Goldenfeld, Phys. Rev. B **48**, 4219 (1993).
19. A. T. Carrington, I. J. Bonalde, R. Prozorov, et al., Phys. Rev. Lett. **83**, 4172 (1999).
20. M. Pinteric, S. Tomic, M. Prester, et al., Phys. Rev. B **66**, 174521 (2002).

Translated by L. Mosina