ISSN 1063-7761, Journal of Experimental and Theoretical Physics, 2021, Vol. 133, No. 1, pp. 104–108. © Pleiades Publishing, Inc., 2021.
Russian Text © The Author(s), 2021, published in Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki, 2021, Vol. 160, No. 1, pp. 126–131.

ELECTRONIC PROPERTIES OF SOLID

Effect of Pressure on the Interlayer Charge Transport and the Electronic Structure of the Metallic Layers in the Organic Two-Dimensional Bilayer Metal $(BETS)_4CoBr_4(DCB)$

R. B. Lyubovskii[a,b], S. I. Pesotskii[a,b,*], V. N. Zverev[c], E. I. Zhilyaeva[a], A. M. Flakina[a], and R. N. Lyubovskaya[a†]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*
[b] *International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, 52-421 Poland*
[c] *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*
**e-mail: pesot@icp.ac.ru*

Received February 10, 2021; revised March 15, 2021; accepted March 18, 2021

Abstract—The resistance and magnetoresistance of the organic $(BETS)_4CoBr_4(DCB)$ metal are studied at atmospheric pressure and a hydrostatic pressure of up to 10 kbar. The interlayer resistance at atmospheric pressure increases with decreasing temperature to $T \approx 25$ K and then decreases as the temperature decreases further. The behavior of magnetoresistance exhibits incoherent transfer over the entire temperature range. The low-temperature metal-like behavior is related to transfer through resonance impurities. Pressure weakens the nonmetallic increase in the resistance and the transfer remains incoherent. The Fourier spectrum of the Shubnikov–de Haas oscillations at atmospheric pressure contains two fundamental frequencies, namely, $F_\alpha \approx 860$ T and $F_\beta \approx 4400$ T, with cyclotron masses $m_\alpha \approx 1.0m_e$ and $m_\beta \approx 1.9m_e$. The applied pressure increases the fundamental frequencies by a few percent, which is most likely to be associated with the pressure-induced decrease in the unit cell size. The cyclotron mass under pressure remains almost the same.

DOI: 10.1134/S1063776121070049

INTRODUCTION

The well-known traditional organic quasi-two-dimensional metals are single-crystal cation-radical salts synthesized using the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecule or its derivatives. During synthesis, layered samples, where cation-radical layers consisting of BEDT-TTF molecules and having metallic conduction along a layer, alternate with nonconducting anion layers [1–3]. As a result, an organic layered metal with an anisotropic conductivity (the ratio of the conductivity of the layer to the conductivity normal to the layer is 10^3–10^4 at room temperature) is synthesized. As a rule, the crystal and electron structures of the neighboring cation-radical layers in a traditional organic metal are the same, and the Fermi surface of each cation-radical layer is the same. An important specific feature of many traditional organic metals is a decrease in both the intra- and interlayer resistance with decreasing temperature [3].

In this work, we study the organic metal $(BETS)_4CoBr_4(DCB)$ (DCB = $C_6H_4Cl_2$), which belongs to a new family of quasi-two-dimensional organic metals, so-called bilayer metals, the properties of which differ significantly from those of traditional organic metals [4, 5]. In these materials, the electronic and crystal structures of the neighboring cation-radical layers are different and the properties of the cation-radical layer are transferred through layers.

An analysis of the structure and properties of $(BETS)_4CoBr_4(DCB)$ revealed the presence of two different alternating radical cation layers [4, 6, 7]. A band structure calculation showed that one of the layers is an insulator with a very narrow energy gap. The second layer is a metal with the Fermi surface characteristic of the θ packing of BETS molecules (see inset to Fig. 2). The investigations of the quantum oscillations in $(BETS)_4CoBr_4(DCB)$ showed good agreement between the frequency spectrum of quantum oscillations with those calculated for traditional θ-packed metals [6, 7]. This spectrum contains the frequencies induced by close-orbit motion and the interference-induced frequencies.

The intralayer resistance of the $(BETS)_4CoBr_4(DCB)$ compound has the specific features of traditional metallic resistance (Fig. 1). However, the temperature dependence of the interlayer resistance shown in Fig. 1 differs significantly from those of most

† Deceased.

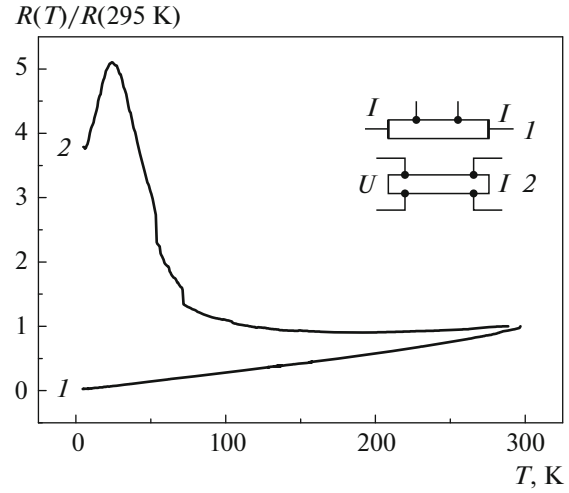

Fig. 1. Temperature dependences of (*1*) intralayer and (*2*) interlayer resistance in $(BETS)_4CoBr_4(DCB)$ at atmospheric pressure [6]. (inset) Schematic geometry of the contacts used to measure (*1*) intralayer and (*2*) interlayer resistance.

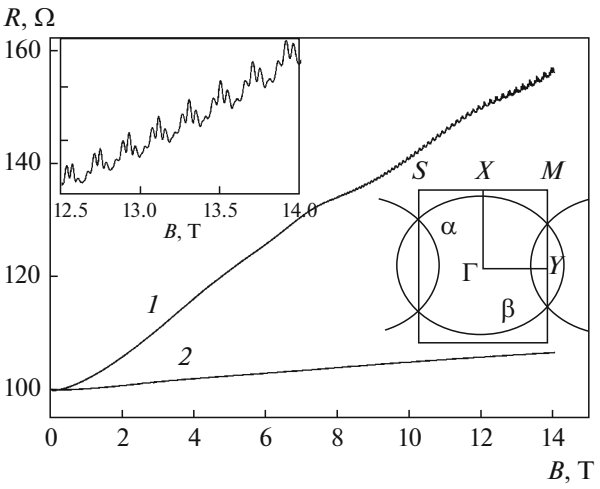

Fig. 2. Field dependences of (*1*) longitudinal and (*2*) transverse interlayer magnetoresistance. The measuring current is perpendicular to the conducting plane, $T = 1.5$ K, and $P = 1$ bar. (left inset) Shubnikov–de Haas oscillations (enlarged part of curve *1* in the field range 12.5–14 T). (right inset) Schematic image of the Fermi surface in $(BETS)_4CoBr_4(DCB)$ [6, 7].

traditional organic layered metals [3]. A similar dependence was observed in some bilayer metals [4].

The change in the temperature dependence of the interlayer resistance at low temperatures is of particular interest. The interlayer electron transfer is usually attributed to the following three modes [2, 3, 8, 9]: coherent, incoherent, and weakly incoherent. In coherent transfer, the electron scattering time τ_c inside a layer is much longer than the time of motion to the neighboring layer, $\tau_z = h/t_z$, where t_z is the transfer integral between layers. Therefore, an electron can pass through many layers before scattering in a certain layer. In this case, the component p_z of the electron momentum is determined, the interlayer transfer has a conventional metallic character, and the entire system is an anisotropic three-dimensional system. In the incoherent mode ($\tau_c \ll \tau_z$), an electron is multiply scattered in a layer before passing to the next layer with a changed momentum. In this case, the component p_z of the electron momentum is undetermined, the electron system has a two-dimensional character, and the interlayer transfer mainly occurs via the jumps induced by the interaction of an electron with lattice defects and phonons. The temperature dependence of the interlayer resistance has a nonmetallic character, and the resistance increases with decreasing temperature.

However, if the transfer integral between the neighboring layers t_z is nonzero, the probability of direct one-particle electron tunneling to the neighboring layer with a retained momentum always exists even in the case of strong scattering inside a layer, $\tau_c \ll \tau_z$. The interlayer resistance ρ_z related to this process has a metallic temperature dependence determined by scattering inside a layer,

$$\rho_z(T) \sim \rho_c(T)\left(\frac{t_c}{t_z}\right)^2\left(\frac{c}{d}\right)^2,$$

where ρ_c and t_c are the intralayer resistance and transfer integral, respectively; c is the lattice parameter in the layer; and d is the interlayer distance [2, 3]. In this case (after single tunneling), an electron is multiply scattered in a layer, the total transfer remains incoherent, momentum p_z is still undetermined, and the system is two-dimensional. This is the so-called weakly incoherent transfer mode. The general temperature dependence of the interlayer resistance under strong scattering inside a layer is determined by the competition between hopping transfer and direct tunneling [10].

These modes have substantially different magnetoresistances [11–13]. In this work, we analyze the temperature and field dependences of magnetoresistance, discuss the interlayer electron transport in the organic two-dimensional bilayer metal $(BETS)_4CoBr_4(DCB)$, and estimate the influence of a hydrostatic pressure of up to 10 kbar on the interlayer transfer and the electronic structure of the metal.

EXPERIMENTAL

We studied single-crystal $1.0 \times 0.5 \times 0.1$ mm^3 parallelepiped samples. The conducting layers were perpendicular to the smallest crystal size. The inter- and intralayer resistances were measured by the standard ac four-probe method, where an alternating current was perpendicular or parallel to the conducting layers.

Taking into account the strong resistance anisotropy, we used different geometries of measuring contacts for different directions (inset to Fig. 1). The magnetoresistance was measured in a superconducting magnet with a maximum field of 15 T using an insert to change the orientation of a sample in a field in both the polar and azimuthal planes without removing a sample fro the magnet. The measurements under pressure were carried out in a high-pressure piston–cylinder cell with a pressure-transferring hydrophobic organic-silicon fluid. Different samples having the same chemical composition were used for investigations at atmospheric pressure and in the high-pressure cell.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the relative interlayer resistance and the resistance along the conducting layers for the $(BETS)_4CoBr_4(DCB)$ single crystal at atmospheric pressure.

The resistance along the layers decreases monotonically by almost two orders of magnitude upon cooling to the liquid-helium temperature, which corresponds to the normal temperature dependence of metal resistance. The interlayer resistance increases monotonically when the temperature decreases to $T_{max} = 25$ K. Further cooling is accompanied by a decrease in the resistance. A nonmetallic type of the temperature dependence on decreasing temperature for bilayer metals is expected. In contrast to traditional organic quasi-two-dimensional metals, the distance between two neighboring identical metallic layers is twice as large ($d \approx 30$ Å [4]), the overlapping of wavefunctions is much smaller, and the transfer integral (t_z) is substantially lower. Thus, the strongly incoherent transfer condition ($\tau_c \ll \tau_z$) is likely to be reliably met, and the interlayer charge transfer is caused by the hopping mechanism and has a nonmetallic temperature dependence down to very low temperatures. However, at a certain interlayer transfer integral, the tunneling to a neighboring layer with a retained momentum is assumed to play a key role in the interlayer transfer at low temperatures, and the temperature dependence of resistance acquires a metallic type characteristic of weakly incoherent electron transport. In this case, temperature T_{max} can be considered as the temperature of changing the interlayer transport mode from incoherent to weakly incoherent.

Figure 2 shows the field dependences of the interlayer magnetoresistance of the $(BETS)_4CoBr_4(DCB)$ compound at atmospheric pressure in a magnetic field, which is perpendicular (longitudinal magnetoresistance) and parallel (transverse magnetoresistance) to the conducting layers, when a measuring current is perpendicular to the conducting layers. The field dependences of the longitudinal magnetoresistance have Shubnikov–de Haas oscillations, which are clearly visible in fields $B > 10$ T. The frequency spectrum of the oscillations contain fundamental frequencies $F_\alpha \approx 860$ T and $F_\beta \approx 4400$ T and a set of combination frequencies [6, 7]. The nonoscillating part of the field dependence of the longitudinal magnetoresistance increases monotonically with the field. The transverse magnetoresistance also increases with the field but by an order of magnitude lower. This behavior of the nonoscillating part of the magnetoresistance in layered metals is characteristic of both incoherent and weakly coherent interlayer electron transport [11–13].

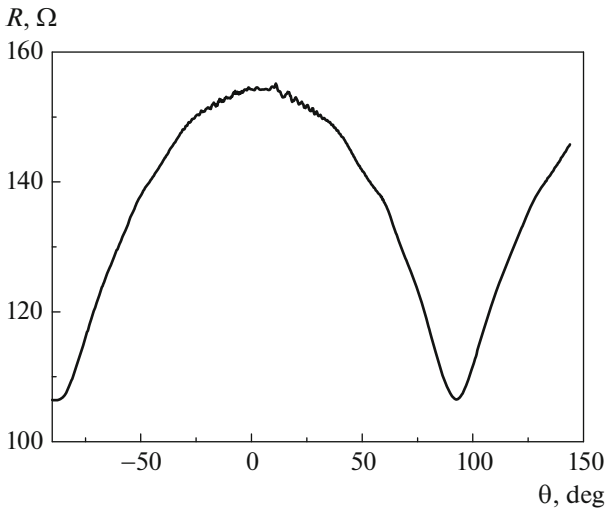

Fig. 3. Angular dependence of the interlayer magnetoresistance in the polar plane. Arbitrary azimuth angle, $T = 1.5$ K, $B = 14$ T, and $P = 1$ bar.

Figure 3 shows the magnetoresistance as a function of the polar angle θ between the field direction and the normal to the conducting layers at atmospheric pressure. The azimuth angle in the conducting layer plane was arbitrary. This dependence remains almost the same when the azimuth angle changes.

A comparative analysis of the angular and field dependences of the magnetoresistance of the $(BETS)_4CoBr_4(DCB)$ compound allows us to draw the following conclusions: (i) the transverse magnetoresistance is isotropic in the azimuth plane and is at most a few percent in the maximum magnetic field, which is parallel to the conducting layers; (ii) the angular dependence in the polar plane is mainly determined by the projection of the field onto the normal to the conducting layers. This behavior of the nonoscillating part of the field dependence of the magnetoresistance is characteristic of both weakly incoherent [14] and incoherent [15] interlayer transport and is related to the uncertainty of momentum component p_z for both modes.

However, semiclassical angular magnetoresistance oscillations (AMRO) in the angular dependence of magnetoresistance at a sufficiently high magnetic field, $\omega_c\tau_c \geq 1$ (where ω_c is the cyclotron frequency),

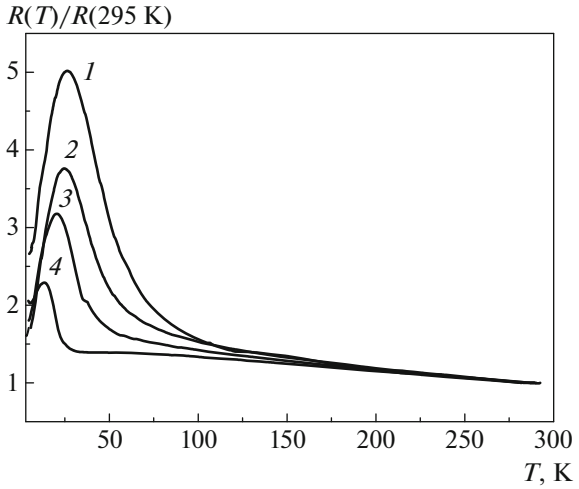

Fig. 4. Temperature dependences of the relative interlayer resistance at a pressure P = (*1*) 0.5, (*2*) 4, (*3*) 7, and (*4*) 10 kbar.

should only be expected for the case of weakly incoherent transfer [11, 12]. In the samples under study, this relation becomes valid in fields $B > 10$ T, which is supported by the observation of Shubnikov–de Haas oscillations in them (see Fig. 2). However, the angular dependences of magnetoresistance have no signs of AMRO even at the lowest temperatures. Thus, the interlayer transfer at temperatures below T_{max} does not correspond to the weakly incoherent mode. Incoherent transfer is most likely to occur in $(BETS)_4CoBr_4(DCB)$ over the entire temperature range from room to liquid-helium temperature. This transfer is assumed to proceed simultaneously along two incoherent parallel channels. The first channel is related to jumps between neighboring layers due to the interaction of electrons with phonons and lattice defects. The resistance of this channel increases when temperature decreases. The second incoherent channel allows electrons to be transferred between layers through resonance impurities with energy levels near the Fermi level of the metallic cation-radical layer [16]. Such impurities should be located between conducting layers.

Calculations in the simplest approximation demonstrate that, at a very low resonance impurity concentration $n_i \ll N$ (where N is the concentration of all other impurity centers), the electrical resistivity of the resonance channel $\rho_i(T)$ is approximately proportional to the intralayer resistivity $\rho_c(T)$ and has a metallic temperature dependence [16]. Since the number of resonance impurities is small, the resistance of the channel at room temperature can be rather high and significantly exceed the resistance of the hopping channel. However, the resistance of the resonance channel at the liquid-helium temperatures decreases by several tens of times and can shunt the resistance of the hopping channel (see Fig. 1).

Thus, the total interlayer resistance at high temperatures is mainly determined by the resistance that increases with decreasing temperature (hopping channel) and that at low temperatures, by the resistance that decreases with decreasing temperature (resonance channel), which leads to the appearance of T_{max}, i.e., the temperature at which the character of the dependence changes.

Figure 4 shows the temperature dependences of the interlayer resistance of $(BETS)_4CoBr_4(DCB)$ at various external hydrostatic pressures. The application of pressure sequentially decreases the nonmetallic increase in the resistance, which appears when temperature decreases. This fact is not surprising, since pressure decreases the distance between metallic layers, increases the transfer integral, and (hence) increases the probability of direct electron tunneling to the neighboring layer. If pressure weakly affects the concentration of resonance impurities, the contribution of these impurities to the interlayer transfer is assumed to be retained at high pressures. This effect is likely to be observed in Fig. 4. The shift of T_{max} toward low temperatures with increasing pressure agrees with this assumption. Thus, an external pressure is likely to weaken the increase in the nonmetallic resistance with decreasing temperature; however, even a pressure $P =$ 10 kbar is too low to suppress the incoherent interlayer transfer in this temperature range (1.5–300 K).

However, a pressure $P = 10$ kbar does not cause qualitative changes in the electronic structure of the metallic cation-radical layers. Figure 5 shows the Fourier spectra of the Shubnikov–de Haas oscillations in $(BETS)_4CoBr_4(DCB)$ at atmospheric pressure and the maximum pressure ($P = 10$ kbar). These spectra are almost identical. (The properties of the quantum oscillations at atmospheric pressure were comprehensively studied in [6, 7].) The spectrum at $P = 10$ kbar contains two fundamental frequencies related to the α and β orbits, $F_\alpha \approx 960$ T and $F_\beta \approx 4700$ T (see inset to Fig. 2), and the corresponding cyclotron masses are $m_\alpha = (1.0 \pm 0.1)m_e$ and $m_\beta = (1.8 \pm 0.1)m_e$, where m_e is the free-electron mass. The combination frequency is also well determined, $F_{\beta-\alpha} \approx 3750$ T. The corresponding cyclotron mass is $m_{\beta-\alpha} = (0.9 \pm 0.1)m_e \approx m_\beta - m_\alpha$. This frequency corresponds to the quantum interference effect [17, 18].

These results demonstrate the absence of qualitative changes in the Fermi surface at a pressure of 10 kbar. The quantitative changes consist of a small (5–10%) increase in the oscillation frequency when the pressure is increased to 10 kbar. This increase can easily be explained by the pressure-induced decrease in the unit cell size and, hence, by the corresponding increase in the unit cell and the Brillouin zone sizes. Since frequency F_β corresponds to the β orbit, which

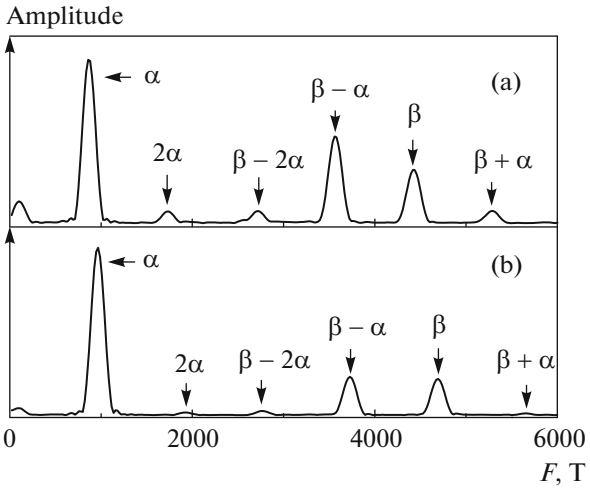

Fig. 5. Fourier spectra of the Shubnikov–de Haas oscillations at P = (a) 1 bar and (b) 10 kbar, $\theta = 0°$, and $T = 1.5$ K.

covers 100% of the first Brillouin zone (two electrons per unit cell) [6], the increase in this frequency does allow us to exactly estimate the increase in the reciprocal unit cell in the conducting plane (which is about 6%). The cyclotron masses under pressure remain unchanged, at least within the limits of experimental error.

CONCLUSIONS

We studied the interlayer resistance and the magnetoresistance of the two-dimensional organic bilayer metal $(BETS)_4CoBr_4(DCB)$ as functions of the temperature, the direction and magnitude of a magnetic field, and the external hydrostatic pressure (up to 10 kbar). The nature of the maximum in the temperature dependence of the resistance was discussed. Arguments for incoherent interlayer electron transfer over the entire temperature range 1.5–300 K were offered. At low temperatures, the transfer is most likely to occur mainly through resonance impurities. The application of an external hydrostatic pressure weakens the increase in the nonmetallic interlayer resistance at high temperatures, and the general incoherent interlayer transfer is retained at all temperatures. The pressure up to 10 kbar does not cause qualitative changes in the electronic structure of the metallic layers. Its influence is restricted to a low quantitative change in the Fermi surface area due to a decrease in the unit cell size.

FUNDING

This work was supported by the Ministry of Education and Science of the Russian Federation (project no. AAAA-A19-119092390079-8), and V.N.Z acknowledges the support of the Russian Foundation for Basic Research (project no. 21-52-12027).

REFERENCES

1. G. Saito and Y. Yoshida, Bull. Chem. Soc. Jpn. **80**, 1 (2007).
2. M. V. Kartsovnik, Chem. Rev. **104**, 5737 (2004).
3. M. V. Kartsovnik, in *The Physics of Organic Superconductors and Conductors*, Ed. by A. Lebed (Springer, Berlin, 2008), p. 185.
4. R. Lyubovskaya, E. Zhilyaeva, A. G. Shilov, et al., Eur. J. Inorg. Chem. **24**, 3820 (2014).
5. T. G. Prokhorova and E. B. Yagubskii, Russ. Chem. Rev. **86**, 164 (2017).
6. R. B. Lyubovskii, S. I. Pesotskii, G. V. Shilov, E. I. Zhilyaeva, A. M. Flakina, and R. N. Lyubovskaya, JETP Lett. **98**, 181 (2013).
7. A. Audouard, J.-Y. Fortin, D. Vignolles, et al., Synth. Met. **226**, 171 (2017).
8. R. H. McKenzie and P. Moses, Phys. Rev. Lett. **81**, 4492 (1998).
9. P. Moses and R. H. McKenzie, Phys. Rev. B **60**, 7998 (1999).
10. D. B. Gutman and D. L. Maslov, Phys. Rev. B **77**, 035115 (2008).
11. P. D. Grigoriev, Phys. Rev. B **83**, 245129 (2011).
12. P. D. Grigoriev, M. V. Kartsovnik, and W. Biberacher, Phys. Rev. B **86**, 165125 (2012).
13. P. D. Grigoriev, Phys. Rev. B **88**, 054415 (2013).
14. M. V. Kartsovnik, D. Andres, S. V. Simonov, et al., Phys. Rev. Lett. **96**, 166601 (2006).
15. R. B. Lyubovskii, S. I. Pesotskii, O. A. Bogdanova, E. I. Zhilyaeva, A. M. Flakina, and R. N. Lyubovskaya, Russ. Chem. Bull. **60**, 1363 (2011).
16. M. V. Kartsovnik, P. D. Grigoriev, W. Biberacher, and N. D. Kushch, Phys. Rev. B **79**, 165120 (2009).
17. L. M. Falicov and H. Stachowiak, Phys. Rev. **147**, 505 (1966).
18. R. W. Stark and C. B. Friedberg, Phys. Rev. Lett. **26**, 556 (1971).