## CONFERENCES AND SYMPOSIA

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Scientific session of the Physical Sciences Division of the Russian Academy of Sciences dedicated to the 60th anniversary of the Zavoisky Kazan Physical-Technical Institute of the Kazan Scientific Center, Russian Academy of Sciences (9 February 2006)

A scientific session of the Physical Sciences Division of the Russian Academy of Sciences (RAS) dedicated to the 60th anniversary of the Zavoisky Kazan Physical-Technical Institute of the Kazan Scientific Center, Russian Academy of Sciences, was held in the Conference Hall of the Zavoisky Kazan Physical-Technical Institute on 19 December 2005. The following reports were presented at the session:

(1) **Krokhin O N** (Lebedev Physics Institute, RAS, Moscow) "50 years of quantum electronics";

(2) **Gorbunov A V, Timofeev V B** (Institute of Solid State Physics, RAS, Chernogolovka, Moscow region) "Bose condensation of interwell excitons and spatial structure of luminescence in lateral traps";

(3) **Chekalin S V** (Institute of Spectroscopy, RAS, Troitsk, Moscow region) "The unique femtosecond spectrometric complex as an instrument for ultrafast spectroscopy, femto-chemistry, and nanooptics";

(4) **Salikhov K M** (Zavoisky Kazan Physical-Technical Institute of the Kazan Scientific Center, RAS) "Timeresolved EPR spectroscopy of nonequilibrium spin systems produced during spin-dependent photophysical and photochemical processes in condensed media";

(5) **Manenkov A A** (Prokhorov General Physics Institute, RAS, Moscow) "The role of electron paramagnetic resonance in the development of quantum electronics: facts and comments";

(6) **Smirnov A I** (Kapitza Institute for Physical Problems, RAS, Moscow) "Magnetic resonance modes in spin-gap magnets";

(7) **Kochelaev B I** (Kazan State University) "Evolution of antiferromagnetic cuprates in high-temperature superconductors";

(8) Garifullin I A (Zavoisky Kazan Physical-Technical Institute of the Kazan Scientific Center, RAS) "The superconductor/ferromagnet proximity effect and its potential application in spintronics."

The main propositions of O N Krokhin's report were published in *Usp. Phys. Nauk* **174** 1117 (2004) [*Phys. Usp.* **47** 1045 (2004)]. A brief presentation of reports 2-6 and 8 is given below.

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## Bose condensation of interwell excitons and spatial structure of luminescence in lateral traps

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We discuss experiments involving direct observations of the collective state in the Bose gas of interacting interwell excitons in double GaAs/AlGaAs quantum wells. In recent years, the possibility of excitonic Bose condensation in quasi-two-dimensional semiconductor systems was actively studied, both experimentally and theoretically [1-16]. These investigations have acquired fundamental significance in connection with impressive achievements in the study of the Bose-Einstein condensation of diluted and deeply cooled atomic gases accumulated in magnetic traps [17]. Among the phenomena studied most thoroughly in experiments are excitons in tunnel-bound double quantum wells in heterostructures [1-3]. In these structures, upon application of a bias voltage in the direction perpendicular to the heterolayers, photoexcited electrons and holes separate to become distributed between the neighboring quantum wells, and are bound together by the Coulomb attraction to make up interwell excitons (Fig. 1). Unlike intrawell excitons, interwell excitons have a dipole moment even in the ground state and cannot combine into exciton molecules or many-particle complexes because of the dipole-dipole repulsion. Interwell excitons are experimentally attractive because they are relatively long-lived: their lifetimes are much longer than the characteristic thermalization times [1, 10]. The Bose condensation of the interwell excitons may be realized only when their free motion is spatially restricted to the planes of the wells, i.e., in lateral traps. In the traps, the interwell excitons are much easier to accumulate at sufficiently low temperatures, and it is thus simpler to realize the critical conditions whereby their Bose condensation may occur [11]. Such traps may be of various origins. For instance, they occur in a natural way in the presence of large-scale fluctuations of the chaotic potential associated with random variations of quantum well widths. The traps for the interwell excitons may be prepared with the aid of inhomogeneous deformations [12] and by producing a strongly

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**Figure 1.** Diagram of optical transitions in heterostructures with double quantum wells (QWs) under a bias voltage applied in the direction perpendicular to the plane of the quantum wells. Optical transition D corresponds to the radiative recombination of a direct (intrawell) exciton and transition I to an indirect (intrawell) exciton.

nonuniform electric field, for instance, employing the tip of a tunnel microscope [13].

Earlier, we demonstrated [3] that in the operation with double quantum wells in n<sup>+</sup>-i-n<sup>+</sup>-GaAs/AlGaAs heterostructures characterized by large-scale fluctuations in the random potential, a very narrow line emerges in the luminescence spectra of interwell excitons in a threshold manner with an increase in optical pumping. The observations were performed through micrometer-sized round holes in a metal mask. With increasing the temperature, the intensity of this line for a fixed pump power lowers, not in the activation manner, but linearly, to a complete disappearance from the spectrum. Experiments of this kind were performed on different high-quality structures, which somewhat varied in architecture and parameters. Nevertheless, the essence of the effect, which involved the threshold emergence of a narrow interwell-exciton luminescence line with increasing the pump power when observations were made through windows in a metal mask, as well as the disappearance of this line by a close-to-linear power law with increasing the temperature, was always reproducible in general. The investigations performed gave grounds to conclude that this effect is associated with the Bose condensation of the interwell excitons in lateral domains (traps) arising from large-scale chaotic fluctuations.

We now address ourselves to an entirely different problem related to the observation of a spatial luminescence structure under the conditions of the Bose condensation of interwell excitons in lateral traps. Recently, this problem was experimentally solved in Ref. [16], where the luminescence of interwell excitons was investigated with a high spatial resolution, with the luminescence excitation and observation effected through variously sized round windows in a metallic mask. The experiments were performed with  $GaAs/Al_xGa_{1-x}As$  heterostructures (x = 0.3) with double GaAs quantum wells 12 nm in width. A four-monolayer AlAs barrier was located between the quantum wells. AlAs barriers of the same thickness were grown at the heteroboundaries between each quantum well and the insulating AlGaAs layers, which were 150 nm thick. The structures were Schottky photodiodes. The role of the inner electrode was played by the two-dimensional electron gas in a broad, 30 nm GaAs quantum well spaced at the distance 150 nm from the double quantum well located deep inside the structure. The two-dimensional electron gas in the broad quantum well appeared due to a silicon-doped delta layer placed near the broad well. A metallic film (a 100 nm thick aluminum layer) sputtered on the heterostructure surface served as an external Schottky gate. A bias voltage was applied between the inner electrode and the Schottky gate.

We first illustrate the quality of the structures with double quantum wells used in our work with the example of the luminescence spectra of interwell and intrawell excitons obtained when the electric voltage across the electrodes was varied (Fig. 1 shows the diagram of optical transitions and Fig. 2 the evolution of the luminescence spectra under variation of the bias voltage). In these experiments, a semitransparent metallic film (the Schottky electrode) covered the entire working area of the structure, and the electric field along the structure surface between the electrodes was rather uniform. Luminescence photoexcitation and observation were effected through a semitransparent metallic electrode. For a bias voltage U > 0.7 V, when a flat-band mode is realized in the structures investigated, the spectrum shows only the intrawell exciton luminescence line D. On application of an electric field, the interwell exciton line I emerges with the width about 1.7 meV. In accordance with the Stark shift of dimensional quantization levels in quantum wells, this line moves towards lower energies as a linear function of the applied bias voltage, while the intrawell exciton line lowers in intensity to eventually disappear from the spectrum. For spectral shifts exceeding the interwell-exciton binding energy by more than an order of magnitude, the intensity of the luminescence line of such excitons remains almost invariable, although their radiative decay time lengthens considerably with the bias voltage. This signifies that nonradiative processes are of little significance in the structures involved and that the structure quality is sufficiently high. Also seen in the luminescence spectra is an intense line with a peak at the energy 1.5143 eV, which corresponds to the direct radiative recombination of two-dimensional electrons in a broad (30 nm) quantum well. This luminescence line lies some distance away from the spectral range of interest and its origin and properties are not discussed here.

Subsequent work was performed with structures that were coated with an opaque metallic film, which played the role of a Schottky gate. Circular windows of various diameters (from 2 to 20  $\mu$ m) were etched in this film using electron-beam lithography; the photoluminescence excitation and recording of interwell and intrawell excitons were effected through these windows. A specifically designed microscopic device enabled observing, through these windows, the spatial luminescence structure with the resolution up to 1  $\mu$ m. The magnified image of the window of a sample, through which the photoexcitation was effected, was projected precisely onto the plane of the



**Figure 2.** Evolution of the photoluminescence spectra of a two-dimensional structure with a double quantum well and a semitransparent electrode deposited atop (a Schottky photodiode) when lowering the voltage across the electrodes from 1.1 V to -1.3 V in 0.05 V decrements. The temperature is T = 1.7 K. The He-Ne laser excitation power is  $P = 1 \mu$ W. The size of the luminescence-exciting laser spot on the sample is 30  $\mu$ m. Indicated are the luminescence lines of intrawell (D) and interwell (I) excitons. The inset shows the current-voltage characteristic of the structure under investigation; for a voltage above 0.7 V, a flat-band mode is realized in the structure.

photosensitive matrix of a cooled silicon CCD camera. The sample was placed into a helium cryostat, which enabled performing the experiments in the 1.6–25 K temperature range. At a temperature T > 4.2 K, the sample was embedded in He<sup>4</sup> vapor. With the aid of interference light filters, it was possible to study the spatial structure of luminescence selectively in spectral composition: either for the interwell excitons or for the intrawell excitons under the same experimental conditions. The photoexcitation was effected with an He–Ne laser and the spectra were recorded using a 'Ramanor-U1000' double monochromator. In all experiments conducted with voltage application, the current through the structure did not exceed 100 nA for the pump power 100  $\mu$ W.

We first consider the experiments in which the window of a structure was projected onto the entrance spectrometer slit and the slit itself extracted only the central part of the window along the diametric line. At the outset, it was determined that the radial distribution of the electric field inside the structure near the window in the metallic mask was strongly nonuniform. The scattered field was lowest at the center of the window and increased in the radial direction towards the mask boundaries. Most importantly, the electric field behaves in a nonmonotonic manner immediately at the annular edge of the window, such that a circular potential well (trap) for interwell excitons along the window perimeter appears. The very fact that a circular potential well emerges near the edges of the window in the metallic mask is experimentally established from the spectral shifts of the interwell exciton luminescence line in the focused excitation scanning near the

window boundaries. The electric field is uniform under the metallic mask itself, but on the whole the field magnitude is smaller than in the region of the circular potential well. The reasons for such behavior of the electric field near the perimeter of the window in the mask, as well as the shape and depth of the circular potential well in relation to the bias voltage and the photoexcitation conditions, will be discussed and published elsewhere.

In the luminescence spectra for a  $5 \mu m$  sized window projected onto the entrance spectrometer slit, observed were bright spots (measuring about  $1.5 \mu m$ ) of interwell exciton luminescence located near the upper and lower edges of the window under investigation, as well as the luminescence of the intrawell excitons (D) at the window center, where the scattered electric field was not high. Figures 3a and 3b show how the narrow line of interwell excitons rises with the pump power against the continuous background, which is associated with localized excitons, when detection is effected under the above conditions. Figures 3c and 3d illustrate how this line vanishes against the continuous background when the temperature is increased from 1.6 to 4.2 K for a fixed pumping. These results are qualitatively equivalent to those published earlier, for instance, in Refs [3, 4].

We now turn to the description of other experiments in which the spot of luminescence from a window of an appropriate size was projected directly onto the detector (a CCD camera) with the resolution up to 1  $\mu$ m, rather than onto a spectral device. In this case, the luminescence of interwell or intrawell excitons was selected with the aid of interference light filters. Under the lowest excitation power,



**Figure 3.** (a) Photoluminescence spectrum of a narrow interwell exciton line as a function of the pump power for a 5  $\mu$ m sized window in a metallic mask (the window is projected onto the entrance spectrometer slit). Values of the excitation power indicated to the right of the curves correspond to the spectra measured at T = 1.7 K. The laser radiation is focused to a spot 30  $\mu$ m in size. (b) Intensity of the narrow interwell exciton line as a function of the pump power; the dashed curve shows a quadratic approximation of intensity versus pump power. (c) Intensity variation of the narrow photoluminescence line with the temperature in the range 1.6-4.2 K for the fixed pump power 5  $\mu$ W; the temperature values indicated to the right of the curves correspond to the spectra. (d) Temperature dependence of the intensity of the narrow luminescence line; the dashed straight line represents a linear approximation of this dependence.

whereby the average density of interwell excitons does not exceed  $10^9 \text{ cm}^{-2}$  (this corresponds to a laser pump with the power about  $1 \,\mu\text{W}$  in a laser spot measuring 50  $\mu\text{m}$ ), the luminescence spot was found to be structureless and the luminescence intensity to be uniformly distributed within the limits of the window [16]. With increasing the pump power, a discrete structure of luminescence spots symmetrically located along the window perimeter appears in a virtually threshold manner: two spots appear initially, then four spots appear with an increase in the pump power, and subsequently six spots appear. The luminescence spots measure about 1.5 –  $2 \,\mu\text{m}$ . For the pump power about 150  $\mu$ W, the number of spots is no fewer than eight, but the structure itself is not clearly resolved. Eventually, for the pump power exceeding  $200 \,\mu\text{W}$ , the discrete structure of luminescence spots smears, turning into a structureless luminescent ring. In the majority of windows investigated, the intensity distribution over the spots in the structure is not strictly axially symmetric: some of the spots can stand out in intensity.

A clear structure of four equidistant luminescence spots is observed in a window measuring 2  $\mu$ m. The luminescence structure in windows measuring 10  $\mu$ m is more complex: apart from the discrete axially symmetric spot structure, a radial ring structure is also observed. In windows measuring 20  $\mu$ m or more, we failed to observe any structure. We emphasize that the spatial luminescence structure in the case of intrawell exciton luminescence is nonexistent in experiments with windows of any size, i.e., the intensity of intrawell exciton luminescence is, under all conditions realized, uniform and practically constant within the limits of the windows.

By the example of a window 5  $\mu$ m in diameter, we investigated the behavior of a temperature-dependent discrete configuration of the hexagonal symmetry made up of six luminescence spots located equidistantly along the perimeter of a circle (Fig. 4). It was found that the effect exhibited a manifestly critical behavior with increasing the temperature for a fixed pumping: specifically, the structure of regularly located luminescence spots began to smear for  $T \ge 4$  K, transforming into a single structureless ring at a temperature about 15 K (Fig. 4e).

It is worth noting that the spatial distributions of intrawell exciton luminescence, which showed up in a near-circular form with a fragmentary axial structure along a ring contour, were earlier observed by Butov et al. [5, 6] in double quantum wells and by Snoke et al. [7, 8] in single quantum wells. Such circular luminescence structures appeared under sufficiently intense focused laser excitation, and the dimensions of the circular structures increased to range into the hundreds of microns with increasing the pump power. They owe their origin to the electron depletion and screening of the applied electric field in the domain of laser pumping, as well as to oppositely directed drifts of electrons and holes that developed under these conditions. Therefore, in our view, there is no direct relation between the experiments in Refs [5-8] and the experiments described in the foregoing, the results of which were reported in Ref. [16].

Our experiments discussed above were carried out on several dozen windows of diameters 2, 5, 10, and 20  $\mu$ m in metallic masks. The spatial configurations of luminescence spots in windows of a fixed size were always reproducible under identical conditions. Therefore, there are no grounds to



**Figure 4.** Spatial structures of interwell exciton luminescence obtained in measurements with a 5  $\mu$ m window in a metallic mask under the pump power 50  $\mu$ W at the temperatures 1.7 K (a), 3.0 K (b), 4.25 K (c), 4.33 K (d), and 15 K (e). (f) Intrawell exciton photoluminescence pattern in a 5  $\mu$ m window for the pump power 50  $\mu$ W and the temperature 1.7 K. The orientation of the sides of each frame corresponds to the directions (110) in the {001} plane of the heterostructure under investigation.

believe that the action of a random potential, which is inevitably present in the samples under investigation, is the prime cause of so regular a formation of the spatially periodic structures of interwell exciton luminescence. In this connection, it is pertinent to note once again that no spatially periodic structures were observed in the case of intrawell exciton luminescence measured under the same experimental conditions.

We now consider other possible causes of the effect under discussion associated with the discovery of spatially periodic, symmetric configurations of interwell exciton luminescence involving luminescence excitation and observation through circular apertures in a metallic mask.

The possibility of the emergence of interwell exciton density waves accompanied by a periodic redistribution of luminescence brightness was predicted in Ref. [18]. However, it is not clear why the period of these waves should change in a stepwise manner with a change in the pump power and why the effect itself should be so critically sensitive to the temperature and the pump on the whole.

Furthermore, in experiments with a focused laser excitation, there always arises a flow of nonequilibrium phonons (a 'phonon wind') from the photoexcitation region, which entrains charge carriers and excitons [19]. Centrally symmetric, spatially extended luminescence patterns, which are reflective of the linear dimensions of the phonon entrainment in the crystal medium, emerge under these conditions; the phonon entrainment magnitude is different for different crystallographic directions [20]. In our case, the pumps are moderate and, most importantly, the temperature criticality of our observed effect is inexplicable on the basis of the phonon wind concept.

The transmission of luminescence radiation through small holes may in principle be affected by surface plasmons of a metallic mask (the polariton effect associated with surface plasmons) [21]. However, with an increase in the window size, this effect is bound to wane and, moreover, the critical behavior under pump and temperature variation should be missing.

Finally, as stated in theoretical paper [15], in the case of attraction between interwell excitons, they can condense into a liquid dielectric phase. By analyzing the nonlinear equation for the exciton density, the author of Ref. [15] arrived at the conclusion that the exciton condensate may have a circular

structure fragmented by equidistantly located droplets of the exciton liquid. However, earlier, in Ref. [9], it was shown that the stability of the interwell-exciton liquid phase under the most optimal conditions is very low. Therefore, the question of stability of the liquid dielectric phase of interwell excitons is still an open question in our opinion.

We believe that the effect discovered has a collective, coherent nature. It occurs in the system of interacting twodimensional interwell excitons in the condensation in a lateral ring-shaped trap. Collective states are characterized by large coherence lengths (over 1 µm) and are destroyed with increasing the temperature due to the destruction of the order parameter. Coherent coupling between the luminescence spots exists and therefore quantum temporal beats should be observable in the conditions of pulsed excitation. The effect has a clearly defined limit on the low-excitationintensity side (low exciton densities) and is not observed when the interwell exciton mobility is below the threshold value defined by the effects of exciton localization in random potential fluctuations. In the strong-pumping domain, the effect also vanishes, which, however, is due to the ionization breakdown of the interwell excitons (the Mott transition). Nevertheless, the pump-power dynamic range within which the effect is observed is rather broad, nearly two orders of magnitude.

In a recently published theoretical paper, Keeling et al. [14] showed that the vortex nature of the condensate produced in the interwell-exciton Bose condensation in a lateral trap manifests itself in the properties of the angular luminescence intensity distribution due to a destructive interference. We emphasize that the expected real-space vortex configurations presented in Ref. [14] are practically identical to our observed patterns of bright luminescence spots equidistantly spaced along the perimeter of a 5 µm window. By way of illustration, we show the far-field photoluminescence patterns obtained from 5 µm windows in a metallic mask, which correspond to the optical Fourier transform of the real spatial structure observed through the window (Figs 5a-5d). The patterns given in Figs 5a and 5b and the patterns given in Figs 5c and 5d pertain to two different windows. The patterns in Fig. 5a and Fig. 5c were obtained for a low pump power (for a below-threshold mobility of the interwell excitons), when the real spatial luminescence intensity distribution in the window is struc-



Figure 5. Far-field photoluminescence intensity distribution patterns obtained through windows in a metallic mask. The patterns correspond to the optical Fourier transform of a real spatial luminescence structure (T = 1.7 K). The pairs of images in Figs 5a and 5b and in Figs 5c and 5d correspond to two different 5  $\mu$ m windows in a metallic mask. The patterns in Figs 5a and 5c were obtained for a low pump power, when the spatial intensity distribution in the window is structureless; the patterns in Figs 5b and 5d were obtained for a substantially higher pump power (about 90  $\mu$ W), when a spatial luminescence structure with the hexagonal symmetry appears in the window, which is similar to the structure shown in Figs 4a-4d.

tureless. In this case, the far-field intensity distribution is also uniform. We emphasize that the concentric interference fringes observed in the far-field patterns are due to diffraction by the exit pupil of the optical system and bear no direct relation to the subject under discussion. The situation is significantly different in the operation with a higher-intensity pump (about 90  $\mu$ W in power), when a spatially periodic luminescence structure with the hexagonal symmetry similar to that shown in Figs 4a-4d is observed in the window. Under these conditions, the far-field patterns depicted in Figs 5b and 5d clearly exhibit the effect of destructive interference (the intensity dip at the center of the far-field pattern), which is qualitatively consistent with the theoretical predictions in Ref. [14]. The above experimental observations are one of the manifestations of the coherence of the collective interwell exciton state in the conditions of Bose condensation in a lateral trap. Furthermore, the discovery of the destructive interference in the far-field patterns is an indication that the luminescence intensity of the condensed exciton phase has a manifest angular directivity relative to the normal to the structure surface, which is a salient feature of superradiance [22]

At the same time, the question of the extent to which the system of interwell excitons is electrically neutral remains open. An attempt to answer this question invites investigations of interwell exciton condensation under the resonance photoexcitation conditions.

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## References

- 1. Fukuzawa T, Mendez E E, Hong J M Phys. Rev. Lett. 64 3066 (1990)
- 2. Butov L V et al. Phys. Rev. Lett. 86 5608 (2001)

- Larionov A V et al. Pis'ma Zh. Eksp. Teor. Fiz. 75 689 (2002) [JETP Lett. 75 570 (2002)]
- Dremin A A et al. Pis'ma Zh. Eksp. Teor. Fiz. 76 526 (2002) [JETP Lett. 76 450 (2002)]; Gorbunov A V, Bisti V E, Timofeev V B Zh. Eksp. Teor. Fiz. 128 803 (2005) [JETP 101 693 (2005)]
- 5. Butov L V et al. Nature 417 47 (2002)
- 6. Butov L V, Gossard A C, Chemla D S Nature 418 751 (2002)
- 7. Snoke D et al. *Nature* **418** 754 (2002)
- 8. Rapaport R et al. Phys. Rev. Lett. 92 117405 (2004)
- Lozovik Yu, Yudson V I Pis'ma Zh. Eksp. Teor. Fiz. 22 556 (1975) [JETP Lett. 22 274 (1975)]; Lozovik Yu E, Berman O L Zh. Eksp. Teor. Fiz. 111 1879 (1997) [JETP 84 1027 (1997)]
- 10. Ivanov A L, Littlewood P B, Haug H Phys. Rev. B 59 5032 (1999)
- 11. Zhu X et al. Phys. Rev. Lett. 74 1633 (1995)
- 12. Snoke D W et al., cond-mat/0410298
- Gorbunov A V, Timofeev V B Pis'ma Zh. Eksp. Teor. Fiz. 80 210 (2004) [JETP Lett. 80 185 (2004)]
- 14. Keeling J, Levitov L S, Littlewood P B Phys. Rev. Lett. 92 176402 (2004)
- 15. Sugakov V I Solid State Commun. 134 63 (2005)
- Gorbunov A V, Timofeev V B Pis'ma Zh. Eksp. Teor. Fiz. 83 178 (2006) [JETP Lett. 83 146 (2006)]
- 17. Ketterle W Rev. Mod. Phys. 74 1131 (2002)
- 18. Chen X M, Quinn J J Phys. Rev. Lett. 67 895 (1991)
- Keldysh L V Pis'ma Zh. Eksp. Teor. Fiz. 23 100 (1976) [JETP Lett.
   23 86 (1976)]; Keldysh L V, Tikhodeev S G Pis'ma Zh. Eksp. Teor. Fiz. 21 582 (1975) [JETP Lett. 21 273 (1975)]
- 20. Greenstein M, Wolfe J P Phys. Rev. Lett. 41 715 (1978)
- 21. Kukushkin I V et al. Phys. Rev. Lett. 90 156801 (2003)
- 22. Dicke R H Phys. Rev. 93 99 (1954)

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## The unique femtosecond spectrometric complex as an instrument for ultrafast spectroscopy, femtochemistry, and nanooptics

## S V Chekalin

## 1. Introduction. Retrospective excursus

Nearly the last forty years of the fifty-year-long history of quantum electronics have been related to ultrashort laser pulses (USPs) [1]. These light 'bullets' occupy a special place in the history of research in ultrafast process dynamics, because they have facilitated the swiftest progress in the measurement of short time intervals over the last several centuries (Fig. 1). The use of USPs enabled real-time investigations of the dynamics of ultrafast processes that had previously been considered 'experimentally unobservable.' Furthermore, the record-high USP power, which allows realizing light fields that are significantly stronger than intraatomic ones, makes the pursuance of unique experiments feasible [1]. The making of the first USP lasers in the USSR was fostered by the prospect of obtaining record-high powers for the solution of the laser fusion problem. Employing a laser facility [2] developed in the Quantum Radiophysics Laboratory in the Lebedev Physics Institute, RAS (FIAN), the first-ever successful experiment on the initiation of a thermonuclear reaction by high-power USP irradiation of a lithium deuteride target was implemented in 1968 [3]. The pulse energy amounted to 20 J for the pulse duration 20 ps. This 25 m long facility, which was the world's highest-power facility at that time, delivered no more than one pulse in



Figure 1. Progress in the measurement of short time intervals during the last four centuries. The inset shows the dynamics of USP duration shortening over a period of 20 years.

15 min, the pulse-to-pulse scatter in the output energy amounting to several hundred percent. The temporal pulse structure was poorly reproducible and the spatial energy distribution in the laser beam was strongly nonuniform due to the multimode radiation nature aggravated by small-scale focusing in the active medium. Nevertheless, also performed at that time were temporal measurements (actually the pioneering measurements of the pump-probe type) to investigate the dynamics of heating and expansion of hightemperature laser-produced plasmas [4] and to observe the emergence and relaxation of refractive index gradients in liquids [5]. Further progress in the USP-assisted investigation of ultrafast processes is associated with the passage to the femtosecond duration range. The subpicosecond structure of USPs was observed even in the first neodymium-glass lasers [6]. The mechanism of femtosecond pulse generation in the radiation self-focusing in the active element [7] was also elucidated at that time. However, subsequent progress in femtosecond technology followed the path of dye lasers. A laser based on self-focusing in an active medium as an instrument of the femtosecond pulse formation was put in operation almost 20 years later [8], and just this kind of solidstate laser (referred to as 'third-generation lasers' [1]) has now gained the widest acceptance.

In 1973, at the Institute of Spectroscopy of the RAS (ISAN), work began on USP applications in scientific research involving picosecond lasers (see Ref. [9] and the references therein). The USSR's first femtosecond USP dye oscillator was put into service at ISAN in 1979 [10]. But it took several additional years to develop the amplifiers and the multichannel recording system required to carry out experiments in ultrafast dynamics with a femtosecond time resolution. Comparing the parameters of the resultant femtosecond laser system with those of the aforementioned USP laser of 1968 shows that apart from shortening the duration (100-300 fs instead of 20 ps), a significant improvement was achieved in the reproducibility of the temporal pulse shape and the output pulse energy (the scatter was within 10%), as was an improvement in uniformity of the beam energy distribution. For the output energy 1 mJ, it was possible to attain at-focus radiation intensities up to  $10^{15}$  W cm<sup>-2</sup>, i.e., of the same order of magnitude as in thermonuclear investigations [3]. However, the radiation selffocusing in the optical elements of the amplifier was responsible for a severe distortion of the temporal pulse profile and the spatial beam energy distribution. Most significant from the standpoint of shortening the duration of experiments was an increase in the 'rate of fire' by almost three orders of magnitude (the pulse repetition rate was several Hertz). Nevertheless, the preparation and pursuance of an experiment at this facility would normally occupy several months (even when working in three shifts).

Several studies of excitation relaxation dynamics were carried out with a femtosecond time resolution at several objects at ISAN in 1985-1995. Investigations were made of energy and charge transfer in bacterial reaction photosynthesis centers [11] and in bacteriorhodopsin [12], photodesorption and selective chromophore photodetachment in molecules adsorbed on a surface [13], the relaxation of photoexcited charge carriers in semiconductor microcrystallites in a glass matrix [14], in polydiacetylene monocrystals [15], and in fullerene [16] and metallic [17] films; the electron-phonon interaction parameter was measured, and an energy gap was observed in high-temperature superconductors [18]. At this stage, the formulation of almost all problems, as well as the interpretation of experimental data, was done by the staff members of the institute. At the end of the 20th century, due to the problem of material and human resources, the outdated equipment was not upgraded and experiments were staged in foreign laboratories. However, due to financial support from the RAS and other organizations, the most modern femtosecond equipment would gradually appear at ISAN, which was collected into a united spectrometric complex within the Collective-Use Center (CUC) organized early in 2004. As different units of this equipment appeared, experiments reliant on new third-generation lasers were resumed at the institute. The experimental capabilities of the complex continue to expand.

## 2. Femtosecond laser complex of the 'Optical and Spectral Research' Collective-Use Center of the Institute of Spectroscopy, RAS

The complex is accommodated in a specially fitted dust-free hall with the temperature stabilized to within 1°C. All equipment is accommodated on vibration-proof optical tables from the Standa company mounted on a common isolated base and is covered with a protective housing, with a low excess pressure maintained inside to keep dust from finding its way into the optical elements (Fig. 2). The complex is comprised of the laser part proper, systems for measuring the pulse parameters, frequency tuning systems, the recording systems for conducting pump-probe type experiments, a photoelectron laser microscope, and auxiliary systems that keep the main units running (power units, cooling units, electronic control units equipped with personal computers, etc.). The main laser components of the complex and their output parameters are diagrammed in Fig. 3. The laser part consists of a 'Tsunami HP' femtosecond pulse oscillator and a 'Spitfire HP' regenerative amplifier made by Spectra Physics. The oscillator is pumped at the wavelength 532 nm by a cw diode-pumped solid-state 'Millenia-V' Nd:YVO<sub>4</sub> laser with the output power 4.5 W. The amplifier is pumped by a pulsed diode-pumped solidstate 'Evolution-X' Nd:YLF laser with the average output power 8 W at the wavelength 527 nm for the pulse repetition rate 1 kHz.



Figure 2. General view of the femtosecond laser complex of the 'Optical and Spectral Research' CUC at ISAN.



Figure 3. Schematic diagram showing the main laser components of the 'Optical and Spectral Research' CUC at ISAN.

It is pertinent to note that third-generation amplifiers use chirped pulse amplification [1], and the limitations normally imposed by self-focusing in the amplifier stages and its associated temporal and spatial pulse distortions are therefore nonexistent in this case. The energy of 800 nm femtosecond pulses at the amplifier output may amount to 1 mJ for the pulse length 45 fs and the repetition rate 1 kHz. The spectral pulse halfwidth (FWHM) is equal to  $\sim 20$  nm. The energy distribution over the beam section is close to the diffraction-limited Gaussian one, the pulse-topulse parameter scatter is within 1%. This parameter is extremely important for stable pulse production in nonlinear frequency conversion and allows obtaining a broad tuning range. The pulse-to-pulse parameter reproducibility is most significant in experiments of the pump-probe type, which involve data averaging over several thousand pulses.

The high beam quality enables the easy production of intensities above  $10^{16}$  W cm<sup>-2</sup> by focusing the pulse at the 800 nm fundamental wavelength. Three parametric amplifier systems afford frequency tuning. Two of them operate in the near-IR range (from 1150 to 8000 nm), the third is a universal 'Topaz' parametric amplifier operating with a continuous

tuning in the spectral range from 240 nm to 10 µm. This parameter combination alone makes this complex unique. We emphasize that the facility's 'rate of fire' is three orders of magnitude higher than that of the previous home-made dye system (six orders of magnitude higher in comparison with the 'rate of fire' of the 1968 facility [2]), apart from quite a substantial broadening of the spectral range. A unique multichannel recording system developed by the Russian 'CDP Systems' company (Troitsk) enables a full realization of these advantages in pump-probe type experiments, which are most often used to study the dynamics of ultrafast processes. The employment of linear diode arrays in lieu of CCDs (charge-coupled devices) for the broadband recording of difference spectra enables operation at the repetition rate 1 kHz (linear CCD arrays can be operated at repetition rates up to several dozen Hertz). This shortens the duration of an experiment by three orders of magnitude in comparison with the time required to carry out the experiment on the previous system.

## **3.** Experiments at the facilities of the Collective-Use Center

Below, we briefly describe the main areas of experiments on the unique spectrometric complex that are underway or planned for the nearest future. These areas can be related to the main objects under investigation.

#### 3.1 Photoelectrons

3.1.1 Laser photoelectron microscope. Schematically, a photoelectron projection microscope is a pointed needle with a curvature radius  $r_c$  placed in a vacuum chamber. A special holder firmly secures the needle at the distance L = 10 cm from the detector, which consists of a microchannel plate and a phosphorescent screen (Fig. 4a). A potential of 0-4 kV is applied to the sample; when this potential is high enough, efficient field (tunnel) emission of electrons from the tip of the needle occurs. The radial electric field directs the emitted electrons to the detector and forms a magnified tip image on the screen. The magnification is given by  $K = L/(br_c)$ , where b is a numerical factor equal to 1.5-2. In the investigation of the photoelectron image of the needle tip, the needle potential is lowered to a level whereby the tunnel electron emission from the tip is zero, such that electrons are emitted strictly due to the external photoeffect in the needle material. As in the case of field emission, the electric field around the tip directs the emitted photoelectrons to the detector to form a photoelectron image of the tip with the same magnification. When ultrasharp ( $r_c = 20 \text{ nm}$ ) nanotips of different materials were irradiated by second-harmonic laser pulses with the wavelength 410 nm, pulse duration  $\approx 60$  fs, repetition rate  $\approx 76$  MHz, and pulse energy 0.03 – 0.3 nJ, their photoelectron images were observed and the resolution about 3 nm was obtained [19]. The measured photocurrent was minimally dependent on the tip potential but was proportional to the squared radiation intensity. No photocurrent was observed under irradiation by the fundamental harmonic pulses of a titanium:sapphire laser (with the wavelength 820 nm and the photon energy 1.56 eV) up to intensity values of the order  $10^9$  W cm<sup>-2</sup>. The above experimental observations are unambiguous indications that the photoelectron images of the tips arise from two-photon emission due to the action of femtosecond laser pulses with



**Figure 4.** (a) Schematic diagram of the photoelectron microscope in the context of the experiment described in Section 3.1.2: I — vacuum chamber, 2 — electrode, 3 — optical fiber, 4 — detector, 5 — TV camera, 6 — special-purpose 'Argus-50' processor, 7 — laser radiation. (b) Distribution of the squared electric field  $E^2$  over the subwave aperture.

the photon energy 3.02 eV. The two-photon photoeffect coefficient was determined for the materials under study. The advantage of this approach in comparison with other 'classic' techniques for measuring the external photoeffect consists in the possibility of obtaining its local values with the spatial resolution as high as 3 nm.

3.1.2 Nonperturbing near-field light measurement. In the experiments in Ref. [20], instead of a nanotip, pointed optical fibers with a metallic coating were used, which had an aperture of the diameter 50-200 nm at the fiber tip transparent to light. These fibers are employed in near-field microscopy. An investigation of the light intensity distribution in a subwave aperture by introducing any sensor into the near-field region is evidently accompanied by a very severe distortion of the initial intensity distribution. For a nonperturbing measurement, the two-photon photoeffect produced by short laser pulses transmitted through the material of the tip was used. In this experiment, femtosecond laser pulses at the wavelength 410 nm were not directed immediately at the tip but were introduced through the other end of the fiber (see Fig. 4). The average power at the waveguide input was limited to a value of 1-3 mW so as not to damage the subwave aperture of the fiber. The light intensity at the fiber output is estimated at  $\sim 10^9$  W cm<sup>-2</sup>. To obtain a  $8 \times 10^4$ -fold magnified image of the tip, a potential of 400-1200 V was applied to the electrode. A quadratic dependence of the photocurrent on the laser radiation power was observed, which was reflective of the two-photon nature of the external photoeffect. The two-photon process efficiency is proportional to the fourth power of the effective electric intensity,  $E^4$ . Figure 4b shows the square root of the

photocurrent intensity as a function of the distance  $\rho$  to the aperture center, i.e., the sought  $E^2(\rho)$  distribution.

3.1.3 Visualization of organic nanocomplexes. In the experiment in Ref. [21] in femtosecond laser projection microscopy of organic nanocomplexes, a quartz 100 nm capillary with a nickel layer vacuum-deposited on it was used as a sharp needle. The photoelectron images of two nickel-coated capillaries with deposited-layer thicknesses 25 and 40 nm (Figs 5a and 5b) were observed when the tip was subjected to femtosecond 400 nm radiation. The external static field produced upon applying a negative 300 V potential to the tip decreased the work function, permitting a one-photon electron emission from the metallic surface to be effected by a light photon with  $\lambda = 400$  nm. In this case, the recorded photoelectron signal was a linear function of the laser radiation energy. At the next stage, the nickel-coated quartz capillary was wetted with an ethanol solution of Cl53 dve molecules and then dried. When this sample was exposed to femtosecond 400 nm radiation, a quadratic dependence of the photoelectron current on the laser pulse energy was observed and the photoelectron image of the organic nanocomplex on the surface of the nanocomplex was recorded with the spatial resolution about 5 nm (Figs 5c and 5d).

An experiment aimed at obtaining a nanolocalized electron beam with a femtosecond duration intended for use in experiments involving reflection from the evanescent wave produced by a femtosecond laser pulse is presently being conducted.

### 3.2 Atoms. Projected experiment in atomic physics

Currently, experiments with atoms are in the preparation stage. Investigations of the spatial localization of an atom in the field of periodic femtosecond laser pulses are planned as joint experiments with the ISAN laboratory headed by V I Balykin. The problem is that the potential that localizes an atom in 'stationary' light traps exerts an appreciable perturbing action on the internal and external atomic degrees of freedom. The calculations in Ref. [22] suggest that it is possible to localize a slow atom in the field of colliding femtosecond pulses with an absolute accuracy ranging into the nanometers. In this case, the localization time can be much longer than the atomic spontaneous decay time and  $10^7-10^8$  times longer than the duration of atomic stay in the laser field.

#### 3.3 Molecules and molecular complexes

3.3.1 Feasibility study of molecular photodissociation by the action of femtosecond IR radiation on overtone vibrations. Femtosecond pulses generated in the near-IR range allow attaining intramolecular selectivity by acting on the vibrational degrees of freedom of molecules in the ground electronic state and by selectively exciting overtones or one of the fundamental vibrations in a shorter time than the characteristic intramolecular vibration redistribution times. This holds some promise that it will be possible to realize photochemical transformations in a molecule that are bondor bond group-selective. In the first experiments [23] conducted jointly with E A Ryabov's laboratory (ISAN), an investigation was made of the decay of CF2HCl molecules in the tuning of femtosecond radiation in the region of the overtone transitions of the  $v_1$  mode (1.3–1.8 µm), as well as at the wavelengths 0.4 and 0.8 µm. The energy of femtosecond pulses at the parametric amplifier output amounted to



Figure 5. Photoelectron images of a quartz 100 nm capillary coated with a nickel layer of thickness (a) 25 nm and (b) 40 nm, and (c) with an organic nanocomplex on the surface of the point. (d) Images of the same complex for a rotated capillary. The structure height at the right of Fig. 5d corresponds to the magnitude of the photoelectron signal.

 $50-130 \mu$ J at the wavelengths  $1.3-1.8 \mu$ m for the pulse duration ~ 100 fs. The radiation was focused in CF<sub>2</sub>HCl at the pressure 1 Torr. The resultant products were analyzed from IR transmission spectra recorded prior to and after the irradiation.

The experiments conducted revealed that the resonances of femtosecond radiation with vibrational overtone transitions at the wavelengths  $\lambda_{0\rightarrow 2} = 1.69$  and  $\lambda_{2\rightarrow 4} = 1.82 \ \mu m$ have little or no effect on the CF<sub>2</sub>HCl decay. Only one final dissociation product  $- CF_3H - was$  discovered, which substantially differentiates the results of CF2HCl dissociation under femtosecond pulse irradiation from the results of thermal pyrolysis under the action of infrared or ultraviolet (UV) nanosecond laser pulses. The absence of the effect of femtosecond radiation resonance with vibrational overtone transitions on the decay of  $CF_2HCl$  may be due to the low intensity of the overtone transitions and the strong anharmonicity of C-H bond vibrations. This is why the cross section of successive multiphoton transitions is very small and the radiation intensity should be high enough to give rise to the excitation and dissociation of the molecule. For the intensity  $\sim 100 \,\mathrm{TW}\,\mathrm{cm}^{-2}$ , the main role in molecular decay is played by field ionization and the contribution of multiphoton excitation becomes insignificant compared with the background of the principal process.

At present, due to the broadening of the IR spectral range of lasers, a start has been made on experiments in selective molecular excitation at the fundamental vibration frequencies of the main bonds.

**3.3.2 Investigation of the dynamics and structure of molecular complexes.** Among the most powerful instruments suited to this purpose are nondestructive optical techniques, which

permit retaining all functional properties of the material under study during investigation. Clearly, the spatial distribution of nanostructure components, as well as the mutual packing of the subunits in the nanostructured material, are critical to the properties of the material as a whole. In turn, information about it can be gained by investigating the relaxation material properties. The nanometer sizes of the subunits suggest that the shortest excitation relaxation times range into the femtoseconds. That is why femtosecond spectroscopy may turn out to be one of the most adequate techniques for investigating and certifying nanostructured materials.

The femtosecond pump-probe technique was used to investigate the dynamics of transmission and reflection difference spectra in two types of objects: in the peripheral pigment-protein complex of the LH2 light-harvesting antenna of the photosynthetic system of the Trs. sibirica purple bacteria (in collaboration with the Belozerskii Institute of Physicochemical Biology, Moscow State University) and in heterophase fullerene-metal nanostructures (jointly with FIAN). The pump-probe technique in its various modifications is the main instrument for the investigation of the femtosecond dynamics of fast processes [9]. The information is gathered in the form of a set of difference transmission and/or reflection spectra (the difference of the logarithms of normalized signals with and without excitation) of a sample recorded with a femtosecond exposure at different time instants prior to and after the excitation of the sample by a femtosecond pulse.

Excitation energy transfer between the LH2-complex absorption bands of Trs. sibirica bacteria under excitation by 800-nm femtosecond pulses. The structural basis of the photosynthetic system of purple bacteria is the pigment-



**Figure 6.** (a) Spectra of the photo-induced optical absorption changes in the LH2 *Trs. sibirica* bacteria complex recorded for different probe pulse delays relative to the excitation pulse. Solid curves show the spectra recorded in the buildup of band bleaching up to the attainment of the strongest effect and the dashed curves show the spectra subsequently recorded during the waning of bleaching. The zero point in time *t* corresponds to the temporal coincidence of the exciting and probing pulse peaks. The spectrum for t = 0 is shown with the bold solid curve. The delay increment is 137 ps. (b) Normalized kinetic curves of the photo-induced optical absorption changes at three wavelengths near the absorption band peaks of the sample.

protein complexes of the reaction center (RC) and of the light-collecting antenna (the LH1 core complex and the LH2 peripheral complex). The main absorption bands of the LH2 complexes under investigation with peaks at wavelengths about 800, 830, and 850 nm are due to absorption by similar bacteriochlorophyll (BCh) molecules. These BCh molecules make up ring structures with a characteristic dimension of the order of several dozen nanometers, which vary mainly in the number and mutual orientation of the BCh. In our case, these structures are denoted as B800, B830, and B850. The spectra of photo-induced optical absorption changes for the LH2 complex under excitation by a 50 fs long pulse at the wavelength 800 nm are presented in Fig. 6 together with the kinetic curves of the changes in optical absorption for different probe wavelengths in the B800, B830, and B850 bands. Despite a strong band overlap and a fast excitation energy transfer between the components of the complex, the obtained kinetic curves show the dependence of the relaxation character on the structure of the object. The



**Figure 7.** Dynamics of the variation in the difference reflection  $\Delta R/R$  (in units of optical density) at the wavelength 1250 nm for C<sub>60</sub>/Sn films, which were deposited in various regimes, under excitation at the wavelength 400 nm.

mathematical data processing and simulations of these experiments performed at Moscow State University revealed a significant difference between the electron structure of the BCh molecular ensemble in the complex investigated and the electron structure in the LH2 complexes in other bacteria.

Ultrafast processes in fullerene-metal nanostructures. Heterophase  $C_{60}$ /Sn nanostructures were fabricated as 50–150 nm films on thin quartz substrates by vacuum deposition from two different sources for the metal and the fullerene. The diagnostics of the samples thus fabricated, which were performed with the aid of X-ray structural analysis, electron microscopy, and optical and Raman spectra, showed that varying the deposition mode allowed obtaining films consisting of (i) fullerene polymers, (ii) 10 nm tin nanocrystals covered with fullerene anions, (iii) oriented submicron-sized tin crystallites (in fact, purely metallic films), and (iv) amorphous structures containing metal fractals.

The kinetic curves (Fig. 7) obtained for the four above structures (the curves are numbered in accordance with the above structure list) exhibit an extremely high sensitivity of the dynamics of ultrafast photo-induced processes in composite media to the quantitative ratio between the components and their spatial packing. The substantial difference between the relaxation processes observed for samples with various geometries of the nanocomposites arises from the distinctions in charge carrier generation and in charge transfer between the metal and the fullerene and back [25]. 640

### 3.4 Ultrafast dynamics in some other structures

3.4.1 Measurement of coherent polarization relaxation times  $T_2$  in condensed media by the femtosecond interference spectroscopy technique. The technique can be applied at a low excitation power and is not complicated by the emergence of a parasitic signal for near-zero delay times, which is commonly inherent in the excitation-probing technique. In the experiment in Ref. [26], a 20 fs long pulse from an oscillator was divided with a Michelson interferometer into two identical collinear pulses of similar intensity and polarization, which were directed onto a sample with a controllable delay. Two coherent polarization waves were generated in the sample, which interfered with each other for a time delay comparable with  $T_2$ . The resultant interference pattern was recorded by a high-sensitivity detector. The capabilities of this technique were demonstrated by the example of two doped-glass samples with a significantly different broadening of the absorption band (500 and 40 nm). Measurements showed that for the broadband sample,  $T_2$  does not exceed the pulse duration (20 fs), and  $T_2 \sim 50$  fs for the narrow-band sample.

3.4.2 Femtosecond dynamics of semiconductor-metal nanostructure cavity modes. The modes of the cavity of a semiconductor film on a metal are a highly sensitive instrument for the detection of ultrafast photo-induced processes at the metal-semiconductor interface [27]. A femtosecond laser pulse gives rise to a photo-induced change in the semiconductor permittivity and hence in the optical thickness of the cavity due to the optical excitation of the semiconductor and/or due to the penetration of electrons into the semiconductor across the Schottky barrier, which results in an ultrafast photovoltaic effect. The change in the metal permittivity under femtosecond irradiation by a laser pulse, which is responsible for an instantaneous change of the cavity boundary conditions, permits observing the generation of photons in a transient resonator (dynamic Casimir effect) and making direct measurements of the dynamics of transient electron tunneling across the barrier (wave-packet tunneling). The experiments are performed by the excitation-probing technique (in collaboration with ISAN laboratories headed by E A Vinogradov and Yu E Lozovik).

Furthermore, the first experiments were carried out to study the effect of femtosecond pulse chirp on the generation of coherent photons in semimetals and narrow-gap semiconductors (jointly with the Institute of Solid State Physics, Chernogolovka).

# **3.5** Experiments in photo-induced material modification and production of optical elements by femtosecond pulse irradiation

*Photo-induced transformations in*  $C_{60}$  *films* irradiated by femtosecond laser pulses were investigated in Ref. [28]. It was found that no photo-induced oxygen uptake into the film is observed under pulsed irradiation, in contrast to the case of continuous irradiation. This has the effect that the photoproducts produced in these two cases are different.

In the interference of femtosecond pulses in light-sensitive media, it has been possible to produce *achromatic holograms*, in which there is no radiation diffraction related to the periodic hologram structure and its attendant dispersion. A start has been made on experiments aimed at the production of these structures in planar waveguides, which will enable fabrication of two-dimensional holographic structures that are one-dimensional mirrors with a complex curvature; they show promise as achromatic integrated optical elements of a new class (jointly with the Central Design Bureau for Unique Instrumentation, RAS) [29].

Experiments aimed at the *formation of Bragg gratings in* optical fibers with the aid of femtosecond UV pulses (jointly with the Fiber Optics Research Center at the Prokhorov General Physics Institute, RAS) [30] and at controllable surface modification [31] are being continued; a start has been made on research into the self-focusing of femtosecond pulses in transparent dielectrics (in collaboration with the Physics Department of Moscow State University) and on experiments aimed at effecting the graphite – diamond phase transition in a high-pressure chamber under femtosecond pulse irradiation (in collaboration with the Institute of High-Pressure Physics, RAS, and FIAN).

## 4. Conclusion

Due to a unique combination of the capabilities of the femtosecond laser complex of the 'Optical and Spectral Research' CUC in ISAN, its uses are by no means limited by the avenues of research discussed above. Moreover, the capabilities of the complex are steadily being broadened: in the immediate future, the output pulse energy will increase to 2 mJ and the pulse duration will shorten to 30 fs (these are actually the limiting parameters for the facilities of this class); terahertz radiation has been obtained, which is planned for use in semiconductor research; more sensitive recording systems with cooled radiation detectors capable of operating in the IR range are under development.

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## References

- 1. Kryukov P G Kvantovaya Elektron. **31** 95 (2001) [Quantum Electron. **31** 95 (2001)]
- 2. Basov N G et al. Zh. Eksp. Teor. Fiz. 57 1175 (1969)
- Basov N G et al. Pis'ma Zh. Eksp. Teor. Fiz. 8 26 (1968) [JETP Lett. 8 14 (1968)]; Basov N et al. IEEE J. Quantum Electron. QE-4 864 (1968)
- Basov N G et al., in *Kvantovaya Elektronika* Vol. 1 (Ed. N G Basov) (Moscow: Sov. Radio, 1971) p. 4 [*Sov. J. Quantum Electron.* 1 (1) 2 (1971)]
- Kryukov P G, Matveets Yu A, Chekalin S V Pis'ma Zh. Eksp. Teor. Fiz. 15 147 (1972) [JETP Lett. 15 101 (1972)]
- Basov N G et al. Zh. Eksp. Teor. Fiz. 65 907 (1973) [Sov. Phys. JETP 38 449 (1974)]
- 7. Zherikhin A N et al. Kvantovaya Elektron. 1 956 (1974) [Sov. J. Quantum Electron. 4 525 (1974)]
- 8. Spence D E, Kean P N, Sibbett W Opt. Lett. 16 42 (1991)
- Letokhov V S et al. Lazernaya Pikosekundnaya Spektroskopiya i Fotokhimiya Biomolekul (Picosecond Laser Spectroscopy and Photochemistry of Biomolecules) (Ed. V S Letokhov) (Moscow: Nauka, 1987); Zherikhin A N, Author's Abstract of Thesis for Candidates Degree (Troitsk: Institute of Spectroscopy, USSR Academy of Sciences, 1981); Sharkov A V, Author's Abstract of

Thesis for Candidates Degree (Troitsk: Institute of Spectroscopy, USSR Academy of Sciences, 1981)

- Matveets Yu A, Semchishen V A Kvantovaya Elektron. 6 848 (1979) [Sov. J. Quantum Electron. 9 503 (1979)]
- Matveets Yu A, Chekalin S V, Yartsev A P Pis'ma Zh. Eksp. Teor. Fiz. 43 546 (1986) [JETP Lett. 43 707 (1986)]; Dokl. Akad. Nauk SSSR 292 724 (1987); Chekalin S V et al. FEBS Lett. 216 245 (1987); Chekalin S V, Matveetz Yu A, Yartsev A P Rev. Phys. Appl. 22 1761 (1987); Matveets Yu A et al. Dokl. Akad. Nauk SSSR 294 1480 (1987); Matveets Yu A, Chekalin S V, Yartsev A P Izv. Akad. Nauk SSSR Ser. Fiz. 53 1462 (1989)
- Matveetz Yu A, Chekalin S V, Sharkov A V J. Opt. Soc. Am. B 2 634 (1985); Sharkov A V et al. Photochem. Photobiol. 38 109 (1983); Sharkov A V et al. Biochim. Biophys. Acta (BBA): Bioenerg. 808 94 (1985); Sharkov A V et al. Dokl. Akad. Nauk SSSR 281 466 (1985)
- Chekalin S V et al. J. Phys. Chem. 92 6855 (1988); Kozlov A A et al. Pis'ma Zh. Eksp. Teor. Fiz. 47 294 (1988) [JETP Lett. 47 353 (1988)]
- Lozovik Yu E et al. Pis'ma Zh. Eksp. Teor. Fiz. 52 851 (1990) [JETP Lett. 52 221 (1990)]; Besel' I V et al. Pis'ma Zh. Eksp. Teor. Fiz. 59 376 (1994) [JETP Lett. 59 403 (1994)]
- Afanas'eva N I et al. Opt. Spektrosk. 82 808 (1997) [Opt. Spectrosc. 82 750 (1997)]
- 16. Bezel I V et al. Chem. Phys. Lett. 218 475 (1994)
- Golovlev V V et al. Pis'ma Zh. Eksp. Teor. Fiz. 55 441 (1992) [JETP Lett. 55 450 (1992)]
- Chekalin S V et al. *Phys. Rev. Lett.* **67** 3860 (1991); Gershenzon M E et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **52** 1189 (1990) [*JETP Lett.* **52** 602 (1990)]; Dobryakov A L et al. *Opt. Spektrosk.* **76** 975 (1994) [*Opt. Spectrosc.* **76** 871 (1994)]
- Sekatskii S K et al. J. Phys. Chem. A 102 4148 (1998); Sekatskii S K et al. Zh. Eksp. Teor. Fiz. 115 1680 (1999) [JETP 88 921 (1999)]; Sekatskii S K et al. Nonlinear Opt. 23 157 (2000)
- 20. Sekatskii S K et al. Appl. Phys. Lett. 83 4900 (2003)
- Aseev S A et al. Pis ma Zh. Eksp. Teor. Fiz. 80 645 (2004) [JETP Lett. 80 568 (2004)]; Mironov B N et al. Zh. Eksp. Teor. Fiz. 128 732 (2005) [JETP 101 628 (2005)]
- 22. Balykin V I Pis'ma Zh. Eksp. Teor. Fiz. 81 268 (2005) [JETP Lett. 81 209 (2005)]
- Apatin V M et al. Pis'ma Zh. Eksp. Teor. Fiz. 80 104 (2004) [JETP Lett. 80 95 (2004)]; Apatin V M et al. Chem. Phys. Lett. 414 76 (2005)
- Razjivin A P et al. Biologicheskie Membrany 22 55, 83 (2005); Kvantovaya Elektron. 35 107 (2005) [Quantum Electron. 35 107 (2005)]
- Chekalin S, Kompanets V, Starodubtsev N Proc. SPIE 6181 282 (2006)
- Kompanets V O, Matveets Yu A, Chekalin S V Kvantovaya Elektron. 31 393 (2001) [Quantum Electron. 31 393 (2001)]
- 27. Vinogradov E A Usp. Fiz. Nauk **172** 1371 (2002) [Phys. Usp. **45** 1213 (2002)]; Laser Phys. **15** 954 (2005)
- Kompanets V O et al. Pis'ma Zh. Eksp. Teor. Fiz. 68 320 (1998) [JETP Lett. 68 344 (1998)]
- Dement'ev D A et al. Pis'ma Zh. Eksp. Teor. Fiz. 65 388 (1997) [JETP Lett. 65 402 (1997)]; Opt. Commun. 150 38 (1998); Aseyev S A et al. Proc. SPIE 6181 274 (2006)
- 30. Zagorulko K et al. Opt. Express 12 5996 (2004)
- 31. Lozovik Yu E et al. *Laser Phys.* **9** 564 (1999)

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## Time-resolved EPR spectroscopy of nonequilibrium spin systems produced during spin-dependent photophysical and photochemical processes in condensed media

## K M Salikhov

#### 1. Introduction

The course of spin-dependent elementary acts may result in the formation of nonequilibrium polarization of electron spins exceeding the equilibrium spin polarization by several orders of magnitude. The physical nature of the nonequilibrium polarization formation is as follows. In elementary photophysical and photochemical events, it is not infrequent that the Hamiltonian of spin systems changes rapidly on a time scale of spin evolution times, and therefore the spins do not follow the variations in the spin Hamiltonian parameters adiabatically. For instance, in the rupture of a chemical bond, two free radicals form that inherit the spin state of the molecule. For these nonadiabatic processes, the disintegration of the molecule is, with respect to the spins of valence electrons, an abrupt switch of the spin Hamiltonian: a large value of the exchange integral in the molecule rapidly gives way to a relatively small value for two radicals at the distance equal to the sum of their Van der Waals radii; the g-factor of unpaired electrons changes simultaneously. The molecular spin Hamiltonian does not commute with the spin Hamiltonian of the two resultant radicals and therefore the electron spins of the radicals at the instant of radical pair production find themselves in a transient coherent state [1]. A similar situation occurs in the photo-induced electron transfer.

The above scheme of the transient spin state formation may formally be represented as follows. We let  $H_1$  and  $\psi_n$ denote the spin Hamiltonian and eigenstates of the system prior to a phototransformation and  $H_2$  and  $\varphi_p$  denote the spin Hamiltonian and eigenstates of the system after the phototransformation.. We assume that the phototransformation occurs in an excited state  $\psi_2$  and the event proceeds nonadiabatically. In this situation, the phototransformation products (for instance, a pair of radicals resulting from molecular photodecay or an electron – hole pair produced in the phototransfer of an electron) are produced in the initial state with the wave function  $\psi_2$ , which is not an eigenfunction for the products because the spin Hamiltonians  $H_1$  and  $H_2$  do not commute, as a rule. This initial state can be represented as a linear superposition of the eigenstates of the products:  $\varphi(0) = \psi_2 = \sum c_p \varphi_p$ . The subsequent evolution of the electron spins is described by the wave function

$$\rho(t) = \sum c_p \exp\left(-\frac{\mathrm{i}E_p t}{\hbar}\right) \varphi_p \,, \tag{1}$$

where  $E_p$  are the energy levels upon phototransformation.

Therefore, by inducing nonadiabatic transformations by a light pulse, it is possible to prepare ensembles of electron spin systems in transient coherent states.

In free-radical or electron-hole pairs, the evolution of wave packet (1) quite frequently proceeds on the nanosecond time scale [1]. Modern techniques of electron paramagnetic resonance (EPR) also permit observing the evolution of transient electron spin states with a nanosecond resolution. Directly observable in EPR experiments is the dipole spin polarization. In the phototransformation of diamagnetic molecules in the initial state  $\psi_2$ , the electron spins are not polarized, and therefore the EPR signal cannot be observed immediately in the products of nonadiabatic reactions. However, the spin dynamics are responsible for the formation of the EPR-observable polarization of electron spins.

We note that elementary photo-induced nonadiabatic reactions allow preparing ensembles of electron spins in the initial states unattainable when starting from the thermodynamic equilibrium. That is why the results of investigations of paramagnets at thermal equilibrium are not directly applicable to the analysis of EPR data obtained in the study of transient photo-induced transformations.

2. Charge separation at the initial stages of photosynthesis Perhaps the most remarkable example of the formation of a nonequilibrium electron spin polarization is the spin behavior of electron-hole pairs produced at the initial stage of solar energy assimilation by photosynthetic systems (see, e.g., Ref. [2]). Charge separation occurs in the reaction center of a photosystem: from a chlorophyll P dimer in a singlet electron-excited state, within a time of 5-6 ps, the electron is transferred to the primary acceptor, a chlorophyll molecule, and then, in a time of the order of 100 ps, to the secondary electron acceptor, quinine Q. This reaction is nonadiabatic and the resultant electron – hole pair  $P^+Q^-$  inherits the singlet spin state of its predecessor, P\*. The distance between the electron and the hole in this pair is about 3 nm, and therefore the spin-spin interaction in frequency units is of the order 10<sup>7</sup> rad s<sup>-1</sup> and manifests itself efficiently only for times longer than  $\sim 10$  ns. For times shorter than 1 ns, this electron-hole pair may be treated as the realization of the Einstein-Podolsky-Rozen-Bohm (EPRB) pair [3]. A very important property of an EPRB pair consists in the spin state of the pair being correlated, although the spin-spin interaction is negligible. This correlation results from the interaction of pair partners in the past, at the P\* dimer.

Therefore, at the primary stage of photosynthesis, electron – hole pairs form in the singlet state:

$$|S\rangle = \frac{|+1/2, -1/2\rangle - |-1/2, +1/2\rangle}{\sqrt{2}}.$$
 (2)

The singlet state is 'dark' for EPR spectroscopy. The recording of EPR is not possible until spin dynamics or paramagnetic relaxation occur. The EPR spectroscopy of the separated charges in the photosynthesis reaction center yields unusual results [4-7]. Some prominent EPR features of the separated charges in the reaction center, which have already been discussed at the scientific sessions of the Physical Sciences Division of the Russian Academy of Sciences [8], are listed below.

(a) The EPR line intensities oscillate and build up with time when experiencing quantum beats with the frequency of singlet-triplet transitions in the electron-hole pair [4, 5, 8].

(b) The EPR spectrum is antiphase in structure: some lines correspond to absorption, other lines to emission [8]. The integral intensity of the EPR spectrum is zero. This signifies that the spin dynamics of an electron-hole pair produce a quadrupole polarization of the pair of electron spins, while the total dipole polarization of the two spins is equal to zero.

(c) The signal of primary spin echo has a phase that depends on the selectivity of spin excitation by the microwave pulses exciting the echo signal. In the case of nonselective spin excitation, the primary spin echo signal turns out to be shifted by  $\pi/2$  relative to the echo signal of the same spin pair upon the establishment of thermal equilibrium [2, 6, 8].

(d) The primary spin echo signal can be obtained with the aid of only one microwave pulse if the electron transfer is initiated by a laser pulse [6, 8]. In this case, the electron transfer reaction produces a pair in spin-coherent state (2). Therefore, in principle, for the formation of a spin echo signal, there is no need for the first microwave pulse, which is intended to produce spins in a coherent state.

Furthermore, other interesting properties were revealed for the ensemble of electron-hole pairs produced in quantum-entangled state (1).

(e) When the microwave field amplitude  $B_1$  is low enough, four antiphase lines are observed in the EPR spectrum, which correspond to single-quantum transitions in the system of two 1/2 spins. With an increase in  $B_1$ , the single-quantum transition lines broaden and a doublequantum transition line shows up at the center of the spectrum [9]. The double-quantum transition line of the spin-correlated pair is of the form of a dispersion curve rather than of an absorption curve [9]. This signifies that the single- and double-quantum transition signals in spincorrelated pairs are shifted by 90° in phase.

(f) Among the promising investigative methods is optical detection of the EPR spectra of spin-correlated electronhole pairs (ODEPR) [10]. The gist of the method is as follows. In the recombination of a pair, recombination luminescence can occur. The intensity of this luminescence depends on the spin dynamics in the pair, specifically on singlet-triplet transitions in the pair. By recording the intensity variation of recombination fluorescence or phosphorescence as a function of the microwave field frequency, it is possible to obtain the ODEPR spectrum of the pair. The doublequantum transition line is missing from the ordinary EPR spectrum when the spins of the pair do not interact. In the ODEPR spectrum of spin-correlated pairs, the doublequantum transition line manifests itself even in the absence of the spin-spin interaction in the pair [11, 12]. Shown in Fig. 1 by way of illustration are the ODEPR spectra calculated for several values of the microwave field amplitude  $B_1$ . The calculations were done for a model situation with the spin-spin interaction in the electron-hole pair assumed to be zero. With increasing  $B_1$ , a narrow doublequantum transition line shows up at the center of the ODEPR electron-hole pair spectrum. For high  $B_1$  values, the peak intensity of the double-quantum transition line in the ODEPR spectrum behaves as  $B_1^4$  and flattens out for high  $B_1$  values [12]. Therefore, a double-quantum transition line may emerge in the ODEPR spectrum of electron-hole pairs even when the spin-spin interaction can be neglected. In this situation, the occurrence of double-quantum transition lines is caused by the spin – spin interaction in the past, prior to the instant of pair production [12].

The manifestations of spin dynamics in the electron – hole pair in the reaction center of photosynthetic systems are just one example of the features of nonequilibrium electron spin polarization in spin-dependent photophysical and photochemical processes. The polarization formation scenario is that as a result of spin-selective molecular process, a spincorrelated pair of paramagnetic particles is formed and a coherent spin state is prepared. The spin dynamics in spincorrelated pairs produce a nonequilibrium polarization of electron spins, which characteristically shows up in EPR experiments.

## 3. Triplet – triplet exciton annihilation

The charge separation in a reaction center is a monomolecular process. The polarization of electron spins may also occur in the course of spin-dependent biomolecular processes. As an example, we mention the mechanism of excited triplet state polarization induced by the mutual annihilation of triplets. It has been known [13] that a pair of interacting excitons in molecular crystals may annihilate due to the



Figure 1. ODEPR spectra for a model system of electron – hole pairs calculated for different values of the microwave field induction  $B_1$ . The calculations neglected the spin – spin interaction, and the difference in g-factors was taken to be equal to 0.02.

energy transfer from one molecule of the pair to the other with the formation of a singlet excited state, resulting in delayed fluorescence. This annihilation of triplets is a spin-selective process.

The polarization of spin S = 1 states is specified by the polarization operators  $T_{LM}$  ( $L = 0, 1, 2; -L \le M \le L$ ) [14]. The operators  $T_{1M}$  define the dipole moment of the triplet:

$$T_{1,+1} = -\frac{S_X + iS_Y}{2},$$

$$T_{1,0} = \frac{S_Z}{\sqrt{2}},$$

$$T_{1,-1} = \frac{S_X - iS_Y}{2}.$$
(3)

The operators  $T_{2M}$  are equivalent to the quadrupole moment tensor

$$Q_{ik} = \frac{1}{2} \left( S_i S_k + S_k S_i - \frac{4}{3} \,\delta_{ik} I \right),\tag{4}$$

where i, k = X, Y, Z and I is the unit operator. For instance,

$$T_{20} = \left(\frac{3}{2}\right)^{1/2} Q_{ZZ} = \left(\frac{3}{2}\right)^{1/2} \left(S_Z^2 - \frac{S(S+1)}{3}\right).$$

The average value of the dipole moment characterizes the integral intensity of the EPR spectrum of the triplet state. The average value of the quadrupole moment characterizes the form of the EPR spectrum [15]. For instance, when the dipole moment is equal to zero and the quadrupole moment is

nonzero, the two lines in the EPR spectrum of a triplet are in antiphase: one line corresponds to absorption (A) and the other to emission (E), i.e., an antiphase EPR spectrum of the A/E or E/A type is expected.

When two triplet excitons meet, their total spin may be equal to 0, 1, or 2. The triplet – triplet annihilation may occur only in singlet pairs. As a result, the triplet pairs that escape annihilation are enriched with the states with the total spin 1 or 2, i.e., in the triplet or quintet states of the pair, respectively. The total spin moment of the pair of colliding triplets A and B is to be denoted by  $\mathbf{S} = \mathbf{S}_A + \mathbf{S}_B$ . Immediately upon collision, the triplet pairs that have escaped mutual annihilation have the density matrix

$$\rho(0) = \frac{1}{9}(P_1 + P_2) \equiv \frac{1}{9} \left\{ \frac{2}{3} \mathbf{S}^2 - \frac{1}{12} \mathbf{S}^4 \right\},\tag{5}$$

where  $P_1 = \mathbf{S}^2 (6I - \mathbf{S}^2)/8$  and  $P_2 = \mathbf{S}^2 (\mathbf{S}^2 - 2I)/24$  are the operators for the projection on the triplet-pair states with the respective total spin 1 and 2. In the state with density matrix (5), the pair of triplets turns out to be spin-correlated. The average value of the scalar product of the spin moments of the pair partners  $\mathbf{S}_A$  and  $\mathbf{S}_B$  is in fact nonzero:

$$\langle (\mathbf{S}_{A}\mathbf{S}_{B}) \rangle = \operatorname{Tr} \left\{ \rho(0)(\mathbf{S}_{A}\mathbf{S}_{B}) \right\} = \frac{2}{9}.$$
 (6)

The subsequent spin dynamics in these spin-correlated pairs form the dipole and quadrupole polarization of each of the triplets of the pair [15]. The spin dynamics in triplet pairs are determined by the spin Hamiltonian that includes the Zeeman interaction of the triplets with the magnetic field  $B_0$ , the energy of splitting in the zero magnetic field (ZFS), and the exchange interaction  $H_{\text{ex}}$  between the triplets:

$$H = \beta g_{A} \mathbf{B}_{0} \mathbf{S}_{A} + \mathbf{S}_{A} \hbar D \mathbf{S}_{A}$$
$$+ \beta g_{B} \mathbf{B}_{0} \mathbf{S}_{B} + \mathbf{S}_{B} \hbar D \mathbf{S}_{B} + H_{ex} , \qquad (7)$$
$$H_{ex} = -\hbar J \left( \frac{1}{2} + 2 \mathbf{S}_{A} \mathbf{S}_{B} \right),$$

where  $g_{A,B}$  are the g-factors of the triplets, D is the ZFS tensor, and J is the exchange integral of the interaction between two triplet excitons in a spin-correlated pair. The principal values -X, -Y, and -Z of the ZFS tensor D are expressed in terms of the parameters D and E: D = (1/2)(X + Y) - Z, E = -(1/2)(X - Y). In this system, the total pair spin  $\mathbf{S}^2 \equiv (\mathbf{S}_A + \mathbf{S}_B)^2$  is not an integral of motion because  $[H, \mathbf{S}^2] \neq 0$ . Consequently, the spin dynamics in spin-correlated pairs of triplets change the total spin of the pair. As a result, the polarization of spins of the pair partners changes.

The spin polarization of the triplet excitons under discussion was first considered in Ref. [15]. We mention some results obtained for short-lived spin-correlated pairs of triplets. The nonzero projection  $\langle S_B \rangle$  of the dipole moment of a triplet exciton on the direction of the external magnetic field shows up in the fourth order of the time-dependent perturbation theory. The dipole polarization of the triplet depends on the crystal orientation in the external magnetic field. For instance, when the magnetic field is aligned with the Z axis of the ZFS tensor, we obtain

$$\langle S_B \rangle = -\frac{16}{27} J \gamma B_0 E^2 t^4 \,, \tag{8}$$

where t is the lifetime of a spin-correlated pair of triplets. When the field is aligned with the X axis of the ZFS tensor, the dipole polarization is

$$\langle S_B \rangle = -\frac{4}{27} J\gamma B_0 (D+E)^2 t^4 \,. \tag{9}$$

A nonzero quadrupole moment of a triplet already appears in the second order of the perturbation theory:

$$\langle Q_{ZZ} \rangle = -\frac{8}{27} DJt^2 , \qquad (10)$$
$$\langle Q_{XX} - Q_{YY} \rangle = -\frac{8}{9} EJt^2 .$$

Therefore, the mutual annihilation of triplets leads to the production of spin-correlated pairs of triplets that have escaped mutual annihilation. The spin dynamics in spin-correlated pairs transforms the mutual ordering of the spins in a pair to the dipole and quadrupole polarization of individual triplets. The necessary condition for the formation of spin polarization caused by triplet-triplet annihilation is the spin-spin interaction between two triplet excitons in a spin-correlated pair. When the distance between the excitons lengthens to the extent that the spin-spin interaction may be neglected, the formation of spin polarization of the triplets ceases. But the separated triplets retain the polarization formed during their encounter and interaction. The manifestation of this spin polarization of the time



**Figure 2.** Time evolution of the low-field  $I_{\rm lf}$  (a) and high-field  $I_{\rm hf}$  (b) components of the EPR spectrum of triplets in a phenazine/tetracyanquinodimethane crystal for T = 300 K. The magnetic field  $B_0$  is parallel to the principal X axis of the ZFS tensor of the triplet exciton.

evolution of the EPR spectra of triplet excitons in mixed molecular crystals [16]. Plotted by way of illustration in Fig. 2 is the time evolution of the intensity of low-field (Fig. 2a) and high-field (Fig. 2b) components in the EPR spectrum of triplet excitons in a phenazine/tetracyanquinodimethane crystal for T = 300 K. It can be seen from Fig. 2 that for the times of the order of 1 µs, the well-known polarization of electron spins of triplet excited states, which emerges due to the spin selectivity of a nonradiative intramolecular singlet – triplet transition [17], manifests itself. And for the times of the order of several dozen microseconds, the nonequilibrium polarization caused by the biomolecular process of triplet – triplet annihilation shows up. Observed in this case is the A/E type spectrum, which is indicative of the emergence of nonequilibrium quadrupole polarization.

## 4. Feasibility of using spin-dependent photo-induced processes in quantum computing

Of great interest is the possibility of using spin-dependent elementary photo-induced events in quantum computing. By way of example, we discuss the feasibility of quantum teleportation of an electron spin state with the quantum communication channel chosen as the spin-correlated electron-hole pairs produced due to photo-induced electron transfer.

Quantum teleportation was shown to be possible in Ref. [18]. Following the general teleportation scheme out-

lined in that work, the following protocol can be used in order to realize the quantum teleportation [19]. We imagine a molecular system containing three characteristic cofactors: A, B, and C. At the first stage, A is reduced, and in the system A<sup>-</sup>BC, the electron spin in the anion radical A<sup>-</sup> is prepared, employing microwave pulses, in a quantumcoherent state in the resonator of a pulsed EPR spectrometer. At the second stage, a light pulse produces the spincorrelated pair  $B^+C^-$  of ion radicals, yielding the three-spin system  $A^{-}B^{+}C^{-}$ . At the third stage, the  $A^{-}B^{+}$  pair should recombine. This recombination is a spin-dependent process. As a rule, recombination is allowed for the singlet spin state in the pair  $A^{-}B^{+}$ . Eventually, we obtain the system ABC<sup>-</sup>, in which the spin of the anion radical  $C^-$  is in the coherent state that is related to the coherent state of the anion radical A<sup>-</sup> by the well-known unitary transformation. According to this protocol, we thus prepare the  $C^-$  electron spin in the coherent state by quantum teleportation of the coherence of another anion radical, A<sup>-</sup>. To measure the coherent state of C<sup>-</sup>, the methods of pulsed EPR spectroscopy can be used. To effect quantum teleportation, a photochemical process can therefore be used to produce the spin-correlated pair  $B^+C^-$ , a quantum communication channel, and to use the recombination of  $A^-B^+$  for the projection of this pair on the singlet state.

To realize the above quantum teleportation protocol, there is good reason to use a natural photosynthetic reaction center (RC) or artificial RC models. A pair of separated charges  $P^+Q^-$  in the RC is a perfect quantum teleportation channel in a system of electron spins. The problem with this approach consists in the inclusion into the system of the reduced  $A^-$ , the carrier of the initial quantum state. Such a modification of the reaction center is basically possible.

## 5. Conclusion

That the electron spins play an important part in the making of chemical bonds has been well known since the emergence of the Heitler – London theory. For a long time, it was believed that the electron spin states are conserved in an elementary chemical event (Wigner's rule). However, time-resolved EPR experiments showed that short-lived intermediate states spin-correlated pairs — form in the course of an elementary photochemical or photophysical event. The spin dynamics in these pairs manifest themselves in the unusual properties of the EPR signal. The study of spin polarization in the course of photo-induced processes has come to be an important part of a new scientific area — spin chemistry [20]. It is hoped that spin-dependent photo-induced processes will also find use in quantum computing.

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## References

- 1. Salikhov K M Chem. Phys. Lett. 201 261 (1993)
- 2. Angerhofer A, Bittl R Photochem. Photobiol. 63 11 (1996)
- 3. Einstein A, Podolsky B, Rosen N Phys. Rev. 47 777 (1935)
- 4. Salikhov K M, Bock C, Stehlik D Appl. Magn. Reson. 1 195 (1990)
- Kothe G et al., in *The Oji Intern. Conf. on Spin Chemistry*, *Tomakomai, Japan, 15-18 July 1991* (Ed. Y J I'Haya) (Tokyo, 1991) p. 420
- Salikhov K M, Kandrashkin Yu E, Salikhov A K Appl. Magn. Reson. 3 199 (1992)
- 7. Salikhov K M, Zech S G, Stehlik D Mol. Phys. 100 1311 (2002)
- (a) Salikhov K M Usp. Fiz. Nauk 160 (4) 77 1990 [Sov. Phys. Usp. 33 299 (1990)]; (b) Salikhov K M, Kandrashkin Yu E Usp. Fiz. Nauk 166 207 (1996) [Phys. Usp. 39 191 (1996)]
- Salikhov K M, Zech S, Stehlik D "Spin dynamics and EPR spectra of charge separated states in photosystem 1", in 30th Congress AMPERE on Magnetic Resonance and Related Phenomena, 23-28 July 2000, Lisbon, Portugal
- 10. Molin Yu N et al. J. Phys. Chem. 84 1853 (1980)
- 11. Salikhov K M, Sakaguchi Y, Hayashi H Chem. Phys. 220 355 (1997)
- 12. Mursalimov L R, Salikhov K M Appl. Magn. Reson. 21 223 (2001)
- 13. Kepler R G et al. *Phys. Rev. Lett.* **10** 400 (1963)
- Varshalovich D A, Moskalev A N, Khersonskii V K Kvantovaya Teoriya Uglovogo Momenta (Quantum Theory of Angular Momentum) (Moscow: Nauka, 1975) [Translated into English (Singapore: World Scientific, 1988)]
- 15. Salikhov K M Appl. Magn. Reson. 26 135 (2004)
- 16. Corvaja C et al. Appl. Magn. Reson. 28 181 (2005)
- 17. Schmidt J Chem. Phys. Lett. 14 411 (1972)
- 18. Bennett C H, Wiesner S J Phys. Rev. Lett. 69 2881 (1992)
- 19. Salikhov K M Proc. SPIE 5833 52 (2005)
- Salikhov K M 10 Lektsii po Spinovoi Khimii (10 Lectures on Spin Chemistry) (Kazan: Unipress, 2000)

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## The role of electron paramagnetic resonance in the development of quantum electronics: facts and comments

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## 1. Introduction

In 2004, the scientific community celebrated two milestones, 60 years of electron paramagnetic resonance (EPR) and 50 years of quantum electronics (QE).

Today, we have one more historic moment to celebrate, 60 years of the Zavoisky Kazan Physical-Technical Institute (KFTI). There is in fact a close historical connection between these three anniversaries. E K Zavoisky's 1944 discovery and the subsequent development — of EPR has fundamentally influenced the making and development of quantum electronics, and the KFTI that bears Zavoisky's name is the leading research institute in the field of EPR. It is this historical connection that served as the stimulus for this paper.

The paper briefly reviews the early development of quantum electronics, including the formulation of its basic principles; the first ammonia-beam quantum oscillator (maser) and the first paramagnetic crystal-based quantum amplifiers (EPR masers); practical EPR maser schemes and their application; and progress from microwave EPR masers to optical quantum oscillators and amplifiers (lasers). The Conferences and symposia

paper also discusses the feedback of QE on research in the field of EPR.

Finally, some historical facts are presented to show the difficulties in perceiving the EPR and QE ideas at the early stage of their development.

## 2. The beginning of quantum electronics

Quantum electronics is generally accepted to have begun in 1954, the publication year of the seminal papers [1, 2] that formulated the basic principles underlying the electromagnetic radiation generation due to stimulated emission of atomic systems in quantum transitions and which reported creating the first QE device, a molecular generator (later called *maser*) operating on a beam of ammonia molecules [2].

The 50th anniversary of QE was widely celebrated in Russia and elsewhere — in particular, at the special topical symposium of the International Quantum Electronics Conference (IQEC) and Conference on Lasers and Electrooptics (CLEO), 17 May, 2004, San Francisco, USA, where the following five talks discussed the history and development of QE:

C H Townes, "Early history of quantum electronics";

N F Ramsey, "Early stimulated emission amplification by an inverted nuclear spin population and H-maser";

N Bloembergen, "Historical comments on the pumping of masers and lasers";

A A Manenkov, "Pages from the history of quantum electronics research in the Soviet Union";

K Shimoda, "Original studies of quantum coherence."

These talks were subsequently published in the *Journal of Modern Optics* (Vol. 52, No. 12, August 15, 2005). Unfortunately, this source is very difficult if not impossible to find in a Russian scientific library.

As is known, quantum amplifiers and oscillators fundamentally hinge on the inversion of energy level population with respect to the thermodynamic equilibrium distribution. The first observations of the inversion were made at the nuclear spin levels of <sup>7</sup>Li in a crystal of LiF (Pound, Purcell, Ramsey, 1950–1951), but they did not lead to the creation of the maser, nor were they recognized as suggesting a new principle for amplifying and generating electromagnetic radiation (for a discussion of these experiments, see Ramsey's San Francisco paper cited above [3]).

The breakthrough came with papers by Basov and Prokhorov [1] and Townes et al. [2], which formulated principles for creating quantum amplifiers and oscillators based on beams of molecules using energy selection in a nonuniform electric field. The first successful realization of these principles used the inversion levels of ammonia molecules [2].

The next key step in the development of QE was to use auxiliary radiation to achieve inversion (Basov and Prokhorov [4], 1955). The idea of the method, as illustrated in Fig. 1 in the case of a three-level system, is that the auxiliary electromagnetic radiation of frequency  $v_{aux}$  induces transitions between the upper and lower levels, producing population inversion between one of these two and an intermediate level, thus creating conditions for the generation at the corresponding transition  $1 \rightarrow 2$  at the frequency  $v_g$ .

Although initially proposed for molecular beams, Basov and Prokhorov's method of auxiliary radiation (commonly known as electromagnetic pumping) turned out to be universal and valid for any atomic system.



**Figure 1.** Schematic of the population inversion using auxiliary radiation (pumping).  $v_{aux}$ , auxiliary radiation frequency;  $v_g$ , signal frequency that provides generation.

In particular, the method was found to be very efficient for inverting the population of the spin levels of paramagnetic ions in crystals, leading to the creation of quantum amplifiers known as EPR masers (Bloembergen [5], 1956). In the first successful realizations of the EPR maser, in 1957–1958, the quantum amplification effect was obtained on transitions in paramagnetic impurity atoms of  $Gd^{3+}$  in ethyl sulfate [6], of  $Cr^{3+}$  in cyanide [7, 8], and of  $Cr^{3+}$  in corundum (ruby) [9].

We note that the very idea of using the spin levels of paramagnetic atoms in a crystal for creating masers benefited from the strides in EPR spectroscopy, as did the successful realization and further development of these devices. As an example, our idea to use ruby as an active maser medium (Manenkov, Prokhorov [10], 1956) was based on EPR studies of this material [11, 12].

In subsequent studies (see monograph [13] for a review), the paramagnetic ion doping technique as a tool to obtain active maser materials was extended to include other crystals ( $Cr^{3+}$ ,  $Fe^{3+}$  in rutile and tungstates,  $Gd^{3+}$  in fluorite, etc).

The studies have shown that ruby is the most efficient maser material owing to its unique combination of spectral, relaxation, dielectric, thermal, and mechanical properties. Ruby masers operating at decimeter and centimeter wavelengths have been developed.

Figure 2 above shows one of the early laboratory mockups of a decimeter ruby maser built in 1958 at the Oscillations Laboratory of the Lebedev Physics Institute, RAS.

## **3.** Applications of EPR masers

Masers as amplifiers of electromagnetic radiation have an extremely low intrinsic noise level (noise in a quantum system is produced by spontaneous emission in the system itself and by thermal emission in the feeder lines [13]). Therefore, immediately following their laboratory realization, EPR masers attracted much attention for application as high-sensitivity microwave detectors in a variety of fields. In the 1960s and 1970s, a series of masers developed in a number of research institutions in the USSR found practical applications in radio astronomy and long-range space telecommunications [14] — work that was awarded the State Prize in 1976. EPR masers were instrumental, in particular, in performing unique experiments for space research.

For example, detailed studies of galactic hydrogen emission at 21 cm and the discovery of new emission lines of highly excited hydrogen in the 8 mm wavelength range (Sorochenko et al. [15], 1969) provided valuable data on the distribution, temperature, density, and dynamics of hydrogen in the galaxy.

Very interesting data on the water content of some space objects were obtained by observing 1.35 cm emission from space (Matvienko et al. [16-18], 1986) following the discovery by Townes et al. [19] in 1969.



**Figure 2.** A decimeter EPR maser built in FIAN at 1958. General view (left) and details: center, a signal waveguide at  $\lambda_c = 15$  cm and a pumping generator at  $\lambda_{pum} = 2.21$  cm; right, two-frequency (signal and pumping) cavity with two feeding waveguides (coaxial for signal, rectangular for pumping).

Finally, planetary radar studies using EPR maser amplifiers have provided new insights into details of what the planets Mercury, Venus, Mars, and Jupiter are like (Kotel'nikov et al. [20], 1962–1964).

# 4. Impact of EPR maser research on the field of EPR

As noted in Section 2, while the EPR maser benefited from progress in EPR spectroscopy, it also provided valuable feedback to the EPR field.

For example, feasibility studies on new crystals for use as active maser media for various wavelength ranges encouraged the development of the EPR spectroscopy of crystals. Also, the study of physical processes in EPR masers (population inversion, saturation effects, transient processes, etc.) stimulated research into relaxation processes in paramagnetic doped crystals.

These studies have provided fundamental insights into EPR spectroscopy and the physics of relaxation phenomena.

Much was learned about the fine and hyperfine structure of the EPR spectra of different crystal classes, more understanding was gained about EPR-line-broadening mechanisms, and new spin-lattice and spin-spin relaxation processes were discovered.

Of particular note are the results concerning relaxation processes in multi-level systems; as noted in Section 2, they are of fundamental importance to the physics of masers in that they determine the possibility of population inversion in a particular material while controlling saturation and transition processes in amplifiers and generators.

Specific aspects of the spin-lattice relaxation in multilevel systems — resonance relaxation processes via intermediate levels — were discovered and analyzed in Refs [21, 22]. Such processes are characteristic of multilevel systems and are observed at low temperatures in many crystals that have iron-group and rare-earth-group paramagnetic ions in their composition.

In this context, interpretations of processes such as the two-step resonance (Orbach et al. [21], 1961), a Raman-type process (Aminov [24], 1962), and a special case of the direct process (Manenkov and Prokhorov [23], 1962) were developed. The last interpretation, commonly accepted as correct,

is schematically illustrated for a three-level spin system in Fig. 3, where wavy lines represent transitions between the corresponding energy levels due to spin-phonon interactions.

Kinetic analysis shows [23] that in the general case, level populations in such a system relax in a very complex (nonexponential) fashion depending on the probabilities of all the transitions involved.

In some special cases, however, population relaxation rates may relate among themselves in a single-exponential way. For example, if the relaxation transition probabilities between the two lower levels are much lower than those between the remaining level pairs ( $w_{12}, w_{21} \ll w_{23}, w_{32}, w_{13}$ ,  $w_{31}$ ), then the system uses level 3 to relax. In another case, when direct relaxation transitions between the upper levels 2 and 3 are much less probable than those between the other level pairs ( $w_{23}, w_{32} \ll w_{12}, w_{21}, w_{13}, w_{13}$ ), level 3 is one through which populations of levels 2 and 3 relax.

Studies of spin – spin relaxation have revealed a variety of multispin cross-relaxation processes that are due to spin – spin interactions, including resonant, harmonic, and combinational [25].

Referring to the illustration in Fig. 4, if the energy differences between the level pairs a, b and a', b' satisfy the condition  $\Delta E_{ab} \approx \Delta E_{a'b'}$ , then spin – spin interactions in such a system give rise to resonant energy exchange between these level pairs (resonant cross relaxation).



**Figure 3.** A three-level spin system. Wavy lines represent transitions due to spin – lattice interactions, with probabilities  $w_{ik}$  (*i*, *k* = 1, 2, 3).



**Figure 4.** Cross relaxation in multilevel spin systems. Arrows indicate transitions due to spin-spin interactions for the resonant (a), combinational (b), and harmonic (c) cross relaxation. m, n, l are the numbers of spins participating in a corresponding cross relaxation process. Panel b, m = 2, n = 2, l = 1; panel c, m = 3, n = 1.

For other relations between the level energies, such as  $m\Delta E_{ab} \approx n\Delta E_{a'b'}$  or  $m\Delta E_{bd} \approx n\Delta E_{ab} + l\Delta E_{cd}$  (where *m*, *n*, *l* are the numbers of spins participating in the corresponding processes), the harmonic or combinational cross relaxation may occur, respectively.

Cross relaxation processes manifest themselves at high concentrations of paramagnetic ions (when spin – spin interactions are important) and appreciably enhance or reduce the possibility and degree of population inversion — and hence the efficiency of quantum amplifiers and generators.

We note that cross relaxation processes are of as much importance to EPR masers as they are to optical quantum amplifiers and generators (lasers), which use doped ion crystals as active media. We note here that cross relaxation processes in optical media have been insufficiently studied. This is especially true for combinational processes. The author knows of no reported observations of such processes in the optical range, although they have been definitely observed in the microwave range (in the system of spin levels of  $Cr^{3+}$  ions in ruby [25]).

## 5. From EPR maser to lasers

The development of microwave EPR masers encouraged extending quantum electronics principles to shorter wavelengths. That the first optical maser (i.e., laser) was realized on a ruby crystal (Maiman [26], 1960) was no chance occurrence. By that time, the physics of the microwave ruby maser was a well-developed field, and optical absorption and luminescence spectra of ruby had been studied in detail [27]. We also note the similarity in structure between the ground and excited states of ruby's  $Cr^{3+}$  ions — the states that determine EPR microwave spectra and optical spectra, respectively.

Importantly, preceding the first laser was an open-type cavity (mirror disk-shaped design) for molecular amplifiers and generators (masers) at submillimeter wavelengths (Prokhorov [28], 1958) — a key achievement that also had a major stimulating effect on research into short-wavelength masers. The first experimental studies of the disk cavity (in the millimeter wavelength range) showed that the open-type cavity allows obtaining high quality factors.

The success of the first ruby laser spurred activity in the field, triggering the effort to create solid-state lasers using doped crystals and glasses and to develop new active laser materials (atomic and molecular gases, semiconductors, liquids, etc.).

EPR and EPR maser studies largely shaped the way in which research into the physics of solid-state lasers developed in such areas as the spectroscopy of impurity ions in crystals, growth of large, optically homogeneous laser crystals, and lasing regimes (e.g., transients). We note that ruby played an especially important role in those studies and is in fact the mainstay QE material, from which highly efficient lasers and microwave masers are made. It is in ruby masers and lasers that physical processes have been most extensively studied, serving as models for describing solid-state masers and lasers in other crystals.

## 6. Some historical context

As any field of science, EPR and quantum electronics have their own complex history of ideas being unwillingly accepted and slowly recognized. What follows is some of my insider stories about the discoverers of EPR and QE.

## E K Zavoisky's story

Historically, the discovery of the EPR phenomenon by E K Zavoisky in 1944 was made in a laboratory at Kazan State University. His first observations of the resonant absorption of electromagnetic radiation, Zavoisky said, were met with skepticism by his immediate colleagues at the Physics Department, and he therefore decided to conduct a special experiment to convince them that this was indeed a resonance effect, and a big one at that. The amplifier's output signal detecting the absorption effect was sent via a power amplifier to a dynamic loudspeaker mounted in the corridor, and Zavoisky then varied the magnetic field of the electromagnet within which the absorption cell of the EPR spectrometer was placed. The trick was that the loudspeaker produced a large volume of sound when the magnetic field was tuned to the electron paramagnetic resonance.

Zavoisky also said that some scientists — including such greats as Landau — did not think too much of his experiment and failed to recognize it as a major discovery — the reason, perhaps, that, even though repeatedly recommended, the discovery never won the Nobel Prize.

#### A M Prokhorov (story excerpt)

"Sometimes Basov and I got a 'you guys are nuts' comment when explaining the idea."

#### E L Feinberg (talk excerpt)

"Nothing fundamentally new here: stimulated emission was predicted by Einstein." (At the FIAN Academic Council session, commenting on the talk by Prokhorov on the idea of using stimulated emission to generate electromagnetic radiation).

## C Townes (story excerpt)

The ideas of QE took some time to gain acceptance even by such great scientists as Niels Bohr and von Neumann. C Townes [30] remembers their immediate reaction to the idea of a quantum generator as told by him. "You must be misunderstanding something," said Bohr. Von Neumann



Figure 5. EPR pioneers: E K Zavoisky (center), S A Altshuler (left), and B M Kozyrev (1968).



Figure 6. Quantum electronics pioneers. Left to right: A M Prokhorov, C Townes, N G Basov (1965).

first reacted in much the same way, "Oh, no, that can't be right. You must be misunderstanding something," but came back in 15 minutes to say, "Hey, you are right."

These two episodes are followed in Townes's book by a passage from Arthur Clarke — the kind of commentary which, the reader may agree, needs no comment:

"People go through four stages before revolutionary development:

- 1) It's nonsense, don't waste my time.
- 2) It's interesting, but not important.
- 3) I always said it was a good idea.
- 4) I thought of it first."

Instead of a conclusion, I hope two historical photographs featuring the pioneers of paramagnetic resonance and quantum electronics will not be out of place (Figs 5, 6).

## References

- 1. Basov N G , Prokhorov A M Zh. Eksp. Teor. Fiz. 27 431 (1954)
- 2. Gordon J P, Zeiger H J, Townes C H Phys. Rev. 95 282 (1954)
- 3. Ramsey N F J. Mod. Optics 52 1647 (2005)

- Basov N G, Prokhorov A M Zh. Eksp. Teor. Fiz. 28 249 (1955) [Sov. Phys. JETP 1 184 (1955)]
- 5. Bloembergen N Phys. Rev. 104 324 (1956)
- 6. Scovil H E D, Feher G, Seidel H Phys. Rev. 105 762 (1957)
- 7. Culver W H Science **126** 810 (1957)
- 8. McWorter A L, Meyer J W, Strum P D Phys. Rev. 108 1642 (1957)
- 9. Zverev G M et al. Zh. Eksp. Teor. Fiz. **34** 1660 (1958) [Sov. Phys. JETP **7** 707 (1959)]
- Prokhorov A M, Manenkov A A, in *High Power Lasers: Science and Engineering* (NATO ASI Ser., Partnership Sub-Series 3, Vol. 7, Eds R Kossowsky, M Jelínek, R F Walter) (Dordrecht: Kluwer Acad. Publ., 1996) p. 585
- 11. Manenkov A A, Prokhorov A M *Zh. Eksp. Teor. Fiz.* **28** 762 (1955) [*Sov. Phys. JETP* **1** 611 (1955)]
- Manenkov A A, Thesis for Candidate of Physicomathematical Sciences (Moscow: P N Lebedev Physics Inst., Acad. of Sciences of the USSR, 1955)
- Karlov N V, Manenkov A A Kvantovye Usiliteli (Itogi Nauki. Ser. Radiofizika. 1964–1965) (Quantum Amplifiers (Progress in Science. Ser. Radiophysics. 1964–1965)) (Ed. A M Prokhorov) (Moscow: VINITI, 1966)
- 14. Manenkov A A, Steinschleiger V B "Kvantovye usiliteli i ikh ispol'zovanie v radiopriemnykh sistemakh dal'nei kosmicheskoi svyazi i radioastronomii" ("Quantum amplifiers and their use in radio receiving systems of long range space telecommunication and radio astronomy"), in *Ezhegodnik Bol'shoi Sovetskoi Entsiklopedii* (Annual of the Large Soviet Encyclopedia) Issue 21 (Editor-in-Chief S M Kovalev) (Moscow: Sov. Entsiklopediya, 1977) p. 566
- Gordon M A, Sorochenko R L Radio Recombination Lines: Their Physics and Astronomical Applications (Astrophys. and Space Library, Vol. 282) (Dordrecht: Kluwer Acad. Publ., 2002)
- Matvienko L I et al. Pis'ma Astron Zh. 6 662 (1980) [Sov. Astron. Lett. 6 347 (1980)]
- 17. Gufrida T S et al. Pis'ma Astron Zh. 7 358 (1981)
- 18. Matvienko L I et al. Pis'ma Astron Zh. 14 468 (1988)
- 19. Cheung A C et al. *Nature* **221** 626 (1969)
- Kotel'nikov V A et al., in *Problemy Sovremennoi Radiotekhniki i* Elektroniki (Problems of Modern Radio Engineering and Electronics) (Ed. V A Kotel'nikov) (Moscow: Nauka, 1980)
- 21. Fin C B, Orbach R, Wolf W P Proc. Phys. Soc. 77 261 (1961)
- Manenkov A A, Milyaev V A, Prokhorov A M Fiz. Tverd. Tela 4 388 (1962) [Sov. Phys. Solid State 4 280 (1962)]
- Manenkov A A, Prokhorov A M Zh. Eksp. Teor. Fiz. 42 1371 (1962) [Sov. Phys. JETP 15 951 (1962)]
- Aminov L K Zh. Eksp. Teor. Fiz. 42 783 (1962) [Sov. Phys. JETP 15 547 (1962)]
- Manenkov A A, Prokhorov A M Zh. Eksp. Teor. Fiz. 42 75 (1962) [Sov. Phys. JETP 15 54 (1962)]
- 26. Maiman T H Nature **187** 493 (1960)
- 27. Sugano S, Tanabe Y J. Phys. Soc. Jpn. 13 880 (1958)
- Prokhorov A M Zh. Eksp. Teor. Fiz. 34 1658 (1958) [Sov. Phys. JETP 7 1140 (1958)]
- 29. Barchukov A I, Prokhorov A M Radiotekh. Elektron. 4 2094 (1959)
- 30. Townes C H J. Mod. Optics 52 1637 (2005)

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## Magnetic resonance modes in spin-gap magnets

## A I Smirnov

In some dielectric crystals with the antiferromagnetic exchange interaction, the projections of spin moments fail to show magnetic ordering even at temperatures approaching absolute zero. Such crystals came to be known as collective paramagnets or spin liquids. Examples of magnetic structures whose spin-liquid ground state is stable to perturbations are quasi-one-dimensional antiferromagnets containing chains of S = 1 spins (Haldane magnets) [1, 2] and chains of S = 1/2 spins with alternating exchange (the exchange integral alternates between  $J \pm \delta$ ), including Peierls spin magnets [3], various dimer spin structures [4], and so-called

spin ladders [5]. Spin-liquid states are singlets and can be either stable or unstable with respect to the transition into an ordered state under small perturbations. For example, crystals with regular S = 1/2 spin states become ordered under an arbitrarily small exchange at temperatures around  $\sqrt{JJ'/k_{\rm B}}$ , where J and J' are the intrachain and interchain exchange integrals, respectively. In the examples of stable spin-liquid systems given above, the system has an energy gap (known as a spin gap) that separates the singlet ground state from excited magnetic states. The system remains stable as long as the perturbation energy per magnetic ion is less than a certain value of the order of the spin gap. In a Haldane magnet, the spin gap has an exchange origin and is equal to 0.41J [2], whereas in an alternating S = 1/2 spin chain, the spin gap is determined by alternation and is equal to  $1.637\delta$  [3].

Spin-liquid ground states are a purely quantum effect and have no classical analogs — unlike antiferromagnetic and ferromagnetic states, for which many properties can be obtained in the molecular field approximation. The susceptibility of a spin-liquid magnet cooled to below the gap temperature drops to zero because magnetic gap excitations 'freeze out.' As a result, the magnetic response of individual magnetic defects shows up well against the background of the nonmagnetic spin-gap matrix and magnetic excitations at low temperatures form a dilute gas.

The subject of this report is the magnetic resonance of collective, exchange-correlated states that occur in spin-gap magnets following the introduction of defects or the thermal activation of excitations.

Earlier, in [6, 7], we reported the formation of unusual clusters in the vicinity of nonmagnetic impurity ions introduced into the spin-gap matrix as a substitute for magnetic ions. In this collective state, spins restore their nonzero average projections near an impurity ion and form nanoscopic regions of local antiferromagnetic order — regions that have their own magnetic moment and a spin that, according to theory and experiment, is S = 1/2 (including the case of Haldane chains of ions with spin S = 1). We now report on a study of dynamic collective states and their interactions with nanoscopic clusters.

Because excitations in exchange-correlated spin chains correspond to spin changing its projection by unity, they must have the effective spin  $S_{\rm eff} = 1$ . This means that transitions between the spin sublevels of these triplet excitations are influenced by the crystal field, resulting in the same splitting pattern as the one known for an isolated magnetic ion with spin S = 1. For this splitting to be observed, these excitations must be isolated from one another. This is indeed the case under the conditions of a concentrated magnet because of the presence of the gap. In Fig. 1, which presents results obtained in Ref. [8], panel (a) shows the increase in the magneticresonant absorption of a ceramic sample of the Haldane magnet PbNi<sub>2</sub>V<sub>2</sub>O<sub>8</sub> for magnetic fields far from the resonance value for the defects described above (for the g-factor 2.0); panel (b) shows zero-field absorption at a frequency about 100 GHz, which indicates that the paramagnetic resonance shifts in frequency due to the effective spin of the triplet excitation interacting with the crystal field. These results, revealing a nonzero frequency of a magnetic resonance of thermally activated excitations in a zero field, imply that triplet excitations in a Haldane magnet have the effective spin S = 1. The existence of a collective spin-gap state in this concentrated magnetic system leads to a situation where the gas of magnetic triplet excitations is dilute, and these excitations interact with the crystal field as isolated spins. This, in turn, results in a magnetic resonance spectrum similar to that of individual spins in a crystal field. We note that in magnetic objects with the effective spin S = 1/2, spin sublevels do not undergo splitting in the crystal field. The fact that absorption is caused by heating suggests that it is due to magnetic excitations with an energy gap; the value of this gap obtained from a neutron diffraction experiment is about 25 K [9]. Temperatures higher than that destroy the correlated Haldane state, turning the magnetic-resonance signal into an ordinary signal of a concentrated paramagnet, whose magnetic resonance spectrum consists of a single line with g = 2.0 (as a result of exchange narrowing). The theory in Ref. [10] predicts that the spin gap splitting by a crystal field in a Haldane magnet is 2D, where D is the single-ion anisotropy constant. The value of this splitting also depends on the wave vector of the triplet excitations: it should decrease as the wave vector moves away from the Brillouin zone boundary, where the frequency of triplet excitations has a minimum [2]. Fitting the absorption spectra observed at 16 K results in the splitting value 86 GHz. At lower temperatures, the magnetic resonance signal of thermally activated excitations cannot be reliably detected, and therefore this value is not necessarily at the bottom of the excitation spectrum: what we see may be transitions between the spin sublevels within a whole group of excitations in a certain region of **k** space.

In samples of  $Pb(Ni_{1-x}Mg_x)_2V_2O_8$ , in which spin chains may be broken as a result of doping, we can trace how traveling triplet excitations interact with spin clusters that form near the ends of broken chains [7]. For this purpose, we examined magnetic resonance signals from clusters and triplets in samples with different impurity concentrations. Figure 2 shows the results in Ref. [11] on the temperature dependence of the resonance field for samples with different impurity concentrations. It is seen that slightly doped samples show well-resolved lines from the resonance defect and thermally activated excitations. Samples with impurity concentrations above 1% show a common collective spin resonance mode for defects and triplet excitations. The frequency of this 'hybrid' magnetic resonance mode is intermediate between those of the cluster resonance and triplet excitation resonance, and its center of gravity shifts to the triplet mode as the temperature is increased due to the exchange narrowing [12] that occurs as the population numbers of the triplet excitations increase.

To observe the effect of the interaction of triplet excitations in spin-gap systems with the crystal field and to examine how the parameters of this resonance depend on temperature, it is more convenient to use single-crystal samples. Figure 3 (from Ref. [13]) shows the magnetic resonance spectrum of crystals of the dimer compound TlCuCl<sub>3</sub>. Line d of the spectrum corresponds to the transition from the singlet ground state to the lowest spin sublevel of the triplet excitation and is best resolved at low temperatures. Lines a, b, and c, which appear on slight heating, correspond to transitions between the (magnetic- and crystal-field-split) spin sublevels of the triplet excitations. We note that in this case, the magnetic ions of the matrix Cu<sup>2+</sup> carry spin S = 1/2, and the effective spin S = 1 of the collective



Figure 1. Absorption at the frequencies 9 GHz (a) and 105 GHz (b) as a function of the magnetic field for ceramic samples of PbNi<sub>2</sub>V<sub>2</sub>O<sub>8</sub> [8].

excited state demonstrates the corresponding splitting in the crystal field. The difference in structure between various resonance modes in Haldane and dimer magnets is that in the former the spin gap corresponds to a wave vector at the Brillouin zone boundary, and therefore direct singlet – triplet transitions are generally impossible to observe in a magnetic resonance experiment. In the dimer magnet TlCuCl<sub>3</sub>, the spin gap corresponds to the zero wave vector, making it possible to observe direct singlet – triplet transitions using the spin resonance method.

The spin sublevels of triplets were found to split in a temperature-dependent manner. Figure 4 (from Ref. [13])

shows how the resonance magnetic fields of the triplet components vary with temperature. As the temperature increases from 1.2 to 4.0 K, splitting undergoes a significant change and assumes an intermediate constant value, but on further increase in temperature the lines come closer together to eventually merge into a single exchange-narrowed line of a concentrated paramagnet at a temperature above the spin gap energy (which is 7.7 K for this compound). That the splitting is temperature-dependent at low temperatures is presumably because the region in **k**-space where triplets are excited becomes larger and because the effective anisotropy parameter of a triplet excitation depends on the wave vector. The



Figure 2. Temperature dependence of the magnetic resonance field for  $Pb(Ni_{1-x}Mg_x)_2V_2O_8$  samples [11].



Figure 3. Magnetic resonance spectrum of the dimer magnet TlCuCl<sub>3</sub> at T = 1.5 K [13].



Figure 4. Resonance fields of components b and c at the frequency 25.94 GHz in the dimer magnet TlCuCl<sub>3</sub> for various temperatures and magnetic field  $\mathbf{H}||b|$ [13].



Figure 5. Energy level diagram of triplet  $\mathbf{k} = 0$  excitations in the dimer magnet TlCuCl<sub>3</sub> [13].

energy level diagram of a triplet of zero-wave-vector excited states in the dimer magnetic TlCuCl<sub>3</sub> is shown in Fig. 5 (from Ref. 13]). Here,  $\Delta$  is the spin gap in the exchange approximation and  $D_0$  and  $E_0$  are the anisotropy parameters of the effective spin Hamiltonian for a spin triplet in a crystal field. We note that in this case, S = 1 excitations arise as collective states in a crystal with spins S = 1/2 at its sites. In the magnetic field  $H_c$  that closes the spin gap for the lower triplet component, the spin-liquid state loses stability, giving way to a magnetic-field-induced antiferromagnetic ordering [14]. The nonlinear dependence of the frequency on the magnetic field signifies the onset of magnetic order and represents a branch of the antiferromagnetic resonance, as discussed in Ref. [13].

To conclude, magnetic resonance experiments have revealed a variety of collective states that are possible for magnetic ions in a singlet matrix of spin-gap crystals: states with the effective spin  $S_{\text{eff}} = 1/2$  at the ends of S = 1 spin chains; excited spin states with the effective spin  $S_{\text{eff}} = 1$  in spin-gap matrices of crystals carrying either spins S = 1 (Haldane systems) or spins S = 1/2 (dimer spin systems); and, finally, hybrid magnetic resonance modes in which nanoscopic clusters and the triplet excitations of a spin-liquid magnet have their spins involved in collective motions.

## References

- 1. Haldane F D M Phys. Rev. Lett. 50 1153 (1983)
- 2. Meshkov S V Phys. Rev. B 48 6167 (1993)
- 3. Pytte E *Phys. Rev. B* **10** 4637 (1974)
- 4. Kageyama H et al. Phys. Rev. Lett. 82 3168 (1999)
- 5. Dagotto E, Rice T M Science **271** 618 (1996)
- 6. Smirnov A I et al. Phys. Rev. B 65 174422 (2002)
- Smirnov A I, Glazkov V N Usp. Fiz. Nauk 172 1313 (2002) [Phys. Usp. 45 1192 (2002)]
- 8. Smirnov A I, Glazkov V N J. Magn. Magn. Mater. 300 216 (2006)
- 9. Uchiyama Y et al. Phys. Rev. Lett . 83 632 (1999)
- 10. Golinelli O, Jolicoeur Th, Lacaze R Phys. Rev. B 46 10854 (1992)
- 11. Smirnov A I et al. J. Magn. Magn. Mater. 272-276 880 (2004)
- 12. Anderson P W J. Phys. Soc. Jpn. 9 316 (1954)
- 13. Glazkov V N et al. Phys. Rev. B 69 184410 (2004)
- 14. Nikuni T et al. Phys. Rev. Lett. 84 5868 (2000)

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## The superconductor/ferromagnet proximity effect and its potential application in spintronics

I A Garifullin

## 1. Introduction

The so-called proximity effect in superconductor/ferromagnet (S/F) systems — or, in other words, the interplay of superconductivity and ferromagnetism in thin-film heterostructures — has been the subject of intense research over the past ten years (see, e.g., Ref. [1]). In the past few years, interest in the effect has grown dramatically because of its potential uses in spintronics (see, e.g., Refs [2-5]). In multilayer thinfilm systems, a certain combination of F and S layers can be created in which the superconducting transition temperature  $T_{\rm c}$  may be controlled by the orientation of the magnetizations of the F layers relative to one another. The authors [2] first used the S/F proximity effect to theoretically design a spin valve for the superconducting current. In their scheme, denoted as S/F1/N/F2, the magnetizations of two ferromagnetic layers F1 and F2 are isolated from each other by a nonmagnetic metallic layer N, sufficiently thin for the superconducting pair wave function to penetrate from layer S to layer F2. In a theoretical design proposed by Tagirov [3], the superconducting layer is in contact with F layers on either side (F1/S/F2 spin valve). Calculations predict that in both structures, the parallel orientation of the F layer magnetizations provides lower  $T_c$  compared with the antiparallel orientation. In order to enable varying the relative orientation of F layer magnetizations, an antiferromagnetic film is usually deposited on the F2 layer, whose anisotropy fields have the effect of fixing the magnetization of the layer — after

which a small external magnetic field can be used to vary the magnetization direction of F1. There is only one recent report on the realization of Tagirov's design of the superconducting spin valve based on the three-layer system CuNi/Nb/CuNi [4]. The difference in  $T_c$  between the parallel and antiparallel arrangements was found to be about 6.0 mK. For the superconducting spin valve to be more effective, it is desirable that the system F1/S/F2 have a property known as 're-entrant superconductivity.' This phenomenon was first observed by us in Fe/V/Fe films in Ref. [6], where we first observed the complete disappearance of superconductivity as the thickness of the Fe layers increased (in the thickness interval 0.5  $< d_{\rm Fe} < 1$  nm) and then saw it restored for  $d_{\rm Fe} > 1$  nm. Another necessary condition for the Tagirov scheme to be effective is that the thickness  $d_s$  of the S layer be comparable to or less than the superconducting coherence length  $\xi_s$ . A natural explanation is that for Cooper pairs to 'feel' the relative orientation of the F magnetizations, the F layer separation must not be too much greater than the size of the Cooper pair, i.e.,  $\xi_s$ . But our study showed that in a standard three-layer F/S/F system, the ferromagnetic film (even a thin one) is so effective in destroying Cooper pairs that the minimum thickness of the S layer for which superconductivity still exists is of the order of  $3\xi_s$  [6, 7]. It was therefore necessary to somehow secure F/S/F superconductivity at  $d_s \sim \xi_s$ , and one possible way to do this was to place a screening layer between the F and S layers.

This talk presents results on the superconducting proximity effect in the thin-film system Fe/Cr/V/Cr/Fe with chromium layers acting as screens [8, 9]. In addition to new results concerning the magnetic phase transition that occurs in a Cr layer as its thickness Cr is varied, we were also able to determine the upper limit for  $d_{Cr}$  for use in a spin valve. We also made an attempt to realize the superconducting spin valve design proposed in Ref. [2]. Our idea (see Ref. [5]) was to replace the virtual layer N between layers F1 and F2 by a real, nonmagnetic intermediate layer intended to introduce antiferromagnetic exchange coupling between the magnetizations of the ferromagnetic layers [10]. This makes it possible to rotate the magnetization directions of layers F1 and F2 by varying their relative orientation from antiparallel to parallel using an external magnetic field and to measure the resulting shift  $\Delta T_c$ . Instead of a three-layer film F1/N/F2, we used a superlattice Fe/V, with F (Fe) layers strongly antiferromagnetically coupled through V layers [11]. This choice was dictated by technology-related practical considerations [12].

## 2. The proximity effect in the Fe/Cr/V/Fe system

We investigated four series of Fe/Cr/V/Cr/Fe samples. Series 1 was used to measure  $d_{Cr}$  at the fixed value  $d_{Fe} = 5$  nm. In the remaining three series (2–4), the thickness  $d_{Cr}$  was fixed and the variable quantity was  $d_{Fe}$ . In all samples, the thickness of the V layer was 30 nm.

The dependence  $T_c(d_{Cr})$  for series 1 is shown in Fig. 1. It can be seen that for  $d_{Cr} < 4$  nm, the superconducting transition temperature increases as the thickness of the chromium layers increases. On further increase in  $d_{Cr}$ , the superconducting transition temperature passes a maximum and then decreases at a much faster rate than that at which it increased to the maximum.

The  $T_{\rm c}(d_{\rm Fe})$  dependences for the samples of the three series with different fixed thicknesses of the chromium layer



Figure 1. Dependence of  $T_c$  on the chromium layer thickness in series 1 at the fixed value  $d_{Fc} = 5$  nm of the iron layer thickness.

 $(d_{Cr} = 1.5, 2.8, 4.7 \text{ nm})$  are shown in Figs 2b-d. It is seen that they are generally similar to the one we previously obtained [6] for three-layer samples of Fe/V/Fe (Fig. 2a). In these samples, the superconducting transition temperature first sharply decreases and then passes a minimum and saturates as  $d_{Fe}$  is increased. In Fe/Cr/V/Cr/Fe samples, the amplitude of the initial drop in  $T_c$  decreases with increasing the thickness of the Cr layers separating the Fe and V layers. At  $d_{Fe} = 4.7 \text{ nm}$ ,  $T_c$  becomes virtually completely independent of  $d_{Fe}$ , apparently due to the screening effect of the Cr layers. As  $d_{Cr}$  increases, fewer Cooper pairs reach Fe layers, thus decreasing the effect of the exchange field of Fe on the superconductivity of the V layer. From these results, the penetration depth of Cooper pairs into the Cr layer was estimated to be 4.0 nm.

This last conclusion contradicts the results in Fig. 1, which clearly show that starting from 4.0 nm - i.e., from thicknesses exceeding the penetration depth of Cooper pairs into chromium layers — the value of  $T_c$  dramatically decreases with  $d_{Cr}$ . This unambiguously signifies that at  $d_{\rm Cr} \sim 4$  nm, the chromium layers themselves dramatically change their properties because Figs 2c, d show that the superconductivity-destroying effect of the Fe layers on vanadium is already screened out at such a thickness of the Cr layer. We believe that the sharp drop in  $T_{\rm c}(d_{\rm Cr})$  at  $d_{\rm Cr} > 4$  nm occurs because of the transition of Cr layers from a nonmagnetic state to the incommensurate spindensity-wave (SDW) state at  $d_{\rm Cr} \sim 4$ . The conclusion that chromium layers less than 4 nm thick are nonmagnetic is in line with Moessbauer experiments [13]. The following argument seems to justify the assumption that the transition of Cr layers to the SDW state leads to the strong suppression of superconductivity. The SDW state is formed in chromium by band electrons, which can also form a proximity-effectinduced superconducting state there. The theoretical study of the coexistence of SDWs and superconductivity (see, e.g., Ref. 14]) showed that in those parts of the Fermi surface where nesting favors the formation of the SDW state, the chance for the superconducting gap to form is slim, and  $T_{\rm c}$ turns out to be reduced if the SDW transition temperature exceeds the initial value of  $T_c$ . Thus, the appearance of the antiferromagnetic order in Cr and the penetration of Cooper



Figure 2.  $T_c$  versus the thickness of iron layers for the samples of series 2–4. The corresponding dependence for the three-layer system Fe/V/Fe is reproduced from Ref. [6] for comparison.

pairs into the Cr layer may be regarded as two competing antagonistic types of collective electron ordering.

# 3. Superconducting properties of vanadium layers deposited on the antiferromagnetically coupled superlattice $[Fe_2V_{11}]_{20}$

Six samples of MgO(100)/[Fe<sub>2</sub>V<sub>11</sub>]<sub>20</sub>/V( $d_V$ ) were prepared for study. In this structure, two monolayers of iron (Fe<sub>2</sub>) separated by 11 monolayers of V (V<sub>11</sub>) played the roles of the ferromagnetic layers F1 and F2. The superlattice [Fe<sub>2</sub>V<sub>11</sub>]<sub>20</sub>, in which these alternating layers were repeated 20 times, was coated by a sufficiently thick layer of vanadium (with the thickness  $d_V$  from 16 to 30 nm). It is known [11] that the  $V_{11}$  layer establishes the antiferromagnetic exchange coupling between Fe<sub>2</sub> layers.

Magnetization measurements showed that the parallel orientation of magnetizations of various Fe<sub>2</sub> layers in the superlattice  $[Fe_2V_{11}]_{20}$  occurs in the magnetic field 6.0 kOe. The superconducting transitions measured resistively had the width around 0.1 K. As one would expect for thin films in a vortex-free state, no noticeable broadening of the transition widths was observed in large magnetic fields. The upper critical field  $H_{c2}$  was determined from the middle of the transition.

It is well known (see, e.g., Ref. [15]) that for an ordinary three-layer system Fe/V/Fe, in which the thick V layer prevents the spin valve effect, the upper critical field for a magnetic field perpendicular or parallel to the film plane closely follows the theoretical prediction for a 2D thin film [16]. For the perpendicular orientation, the upper critical field is linear in temperature, and in the parallel case the observed dependence is given by

$$H_{c2}^{\rm par} = \frac{\Phi_0}{2\pi\xi(0)} \frac{\sqrt{12}}{d_{\rm s}} \sqrt{1 - \frac{T}{T_{\rm c}}},$$

where  $\Phi_0 = 2 \times 10^{-7} \text{ G cm}^2$  is the magnetic flux quantum,  $\xi(0)$  is the Ginzburg–Landau superconducting coherence length at T = 0 K, and  $d_s$  is the thickness of the superconducting layer. Figure 3 presents the temperature dependences of the square of the upper critical field  $H_{c2}^{par}(T)$  for samples of  $[Fe_2/V_{11}]_{20}/V(d_V)$ . It is seen that the temperature dependence is ideally described by a straight line at fields above 6.0 kOe and increasingly deviates from it below 6.0 kOe. Extrapolating the straight line yields a superconducting transition temperature that is lower than the measured zero-magnetic-field value by more than 0.1 K. A comparison with the magnetization curve of the superlattices  $[Fe_2/V_{11}]_{20}$ shows that the value 6.0 kOe at which the F layer magnetizations turn out to be parallel correlates well with the onset of the linear dependence of  $(H_{c2}^{par}(T))^2$ . This suggest that the deviation in the behavior of the upper critical field from the 2D behavior is due to the gradual change in the relative orientation of the sublattice magnetizations in the superlattice  $[Fe_2/V_{11}]_{20}$  from the parallel orientation in the field above 6.0 kOe to the antiparallel in the zero field. For the sample with  $d_{\rm V} = 16$  nm, the superconducting transition temperature is  $T_c = 1.78$  K, whereas extrapolation from the region of ferromagnetic saturation yields  $T_c = 1.67$  K. Analysis shows that the 0.11 K difference in  $T_c$  is due to the superconducting effect of the spin valve.

## 4. Conclusion

The study of the proximity effect in a thin-film layered system Fe/Cr/V/Cr/Fe clearly demonstrates the strong screening effects of the Cr layers placed between the superconducting layer of V and the Fe layers that destroy the Cooper pairs. At the chromium layer thickness  $d_{\rm Cr} > 4$  nm, the layers of iron already have practically no effect on  $T_{\rm c}$  for vanadium. From this fact, the upper limit of the penetration depth of Cooper pairs into Cr layers is determined to be 4.0 nm. If the chromium layers behaved as a normal nonsuperconducting metal — for example, Cu — then the penetration depth would reach micrometer values at low temperatures. In chromium



**Figure 3.** The square of the parallel upper critical field as a function of the temperature for the samples  $[Fe_2V_{11}]_{20}/V$  (16 nm) (a) and  $[Fe_2V_{11}]_{20}/V$  (30 nm) (b). Solid line is the linear extrapolation of the temperature dependence from the region of large fields.

layers, the penetration depth of the superconducting pair wave function is determined by electron scattering from defects with an uncompensated local magnetic moment. This effect — the strong screening by chromium layers of the exchange field created by the F layer — will hopefully be used in our further attempts to realize the Tagirov spin valve design.

We have also examined the superconducting spin valve effect in a layer of V deposited on an antiferromagnetically coupled lattice [Fe/V]. Our experiments showed that the superconducting transition temperature of a vanadium film is very sensitive to the relative orientation of the Fe<sub>2</sub> layers of the antiferromagnetically coupled superlattice [Fe<sub>2</sub>/V<sub>11</sub>]<sub>20</sub>. Clearly, F layers in our system cannot be switched easily from the antiparallel to the parallel state because this transition occurs gradually as the external magnetic field is varied from 0 to 6.0 kOe. Still, we hope that it is possible to build a switching devise by replacing the antiferromagnetically coupled superlattice [Fe<sub>2</sub>/V<sub>11</sub>]<sub>20</sub>.

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## References

- 1. Buzdin A I Rev. Mod. Phys. 77 935 (2005)
- 2. Sanjiun Oh, Youm D, Beasley M R Appl. Phys. Lett. 71 2376 (1997)
- 3. Tagirov L R Phys. Rev. Lett. 83 2058 (1999)
- 4. Gu J Y et al. Phys. Rev. Lett. 89 267001 (2002)
- 5. Westerholt K et al. Phys. Rev. Lett. 95 097003 (2005)
- 6. Garifullin I A et al. *Phys. Rev. B* **66** 020505 (2002)
- 7. Lazar L et al. Phys. Rev. B 61 3711 (2000)
- 8. Garifullin I A et al. Phys. Rev. B 70 054505 (2004)
- Garifullin I A et al. Pis'ma Zh. Eksp. Teor. Fiz. 80 50 (2004) [JETP Lett. 80 44 (2004)]
- 10. Bruno P, Chappert C Phys. Rev. B 46 261 (1992)
- 11. Hjörvarsson B et al. Phys. Rev. Lett. 79 901 (1997)
- 12. Isberg P et al. Vacuum 48 483 (1997)
- 13. Almokhtar M J. Phys.: Condens. Matter 12 9247 (2000)
- 14. Machida K J. Phys. Soc. Jpn. 50 2195 (1981)
- 15. Wong H K et al. J. Low Temp. Phys. 63 307 (1986)
- 16. de Gennes P G, Tinkham M Physics 1 107 (1964)