EPR study of superconductors

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(Dated: October 14, 2014)

Historical review on the studies of the electron paramagnetic resonance in superconductors performed in the period from 1970 to 1990 at the Kazan Physical Technical Institute of the Russian Academy of Sciences (group of Dr. E. G. Kharakhsh’yan) in collaboration with Kazan State University (group of Prof. B. I. Kochelaev) and with the Institute for Physical Problems of Russian Academy of Sciences (group of Prof. N. E. Alekseevskii) is presented. We have observed for first time electron paramagnetic resonance of impurities in a type II superconductor; found indication for a long-range exchange interaction between magnetic impurities arising due to the superconducting correlations; observed the magnetic ordering of impurities in the superconducting state; and, finally, we found one of the first evidences for heterogeneity of the 1:2:3 high-$T_c$ superconductor which is its natural property.

I. INTRODUCTION

Superconductivity is a striking physical phenomenon; it is a manifestation of quantum effects on a macroscopic scale. The most striking features of superconductivity are (i) the zero value of the electrical resistivity, (ii) the expulsion of the magnetic flux (Meissner effect), (iii) the interference between macroscopically separated junctions. None of these phenomena can be studied using any magnetic resonance method because the basic properties of superconductivity are the quantum effects on a macroscopic scale, while magnetic resonance is a microscopic tool. Therefore, the properties of superconductors from magnetic resonance were not expected to be striking as the above mentioned effects. However, it was expected that they can help to investigate the microscopic aspects of superconductivity. In particular, these are the superconducting coherence phenomena, the superconducting and magnetic correlations.

Significant role of the nuclear magnetic resonance (NMR) studies of superconductors is well known. Indeed, one of the first experimental confirmations of the validity of microscopic theory derived by Bardeen-Cooper-Schrieffer (BCS)1 was obtained by NMR. Hebel and Slichter2 have shown experimentally that the nuclear spin relaxation time $T_1$ just below the superconducting transition temperature $T_c$ is shorter than in the normal state. That is the direct evidence of validity of BCS theory. This happens (see, e.g.,3) due to the opening up of the superconducting gap when the total number of states is a constant, the density of states of conduction electrons at the Fermi level $\rho(E_F)$ averaged over an energy interval of about $k_BT$ (for $T \approx T_c$) is larger in the superconducting state than in the normal state. Therefore, the shortening of $T_1$ just below $T_c$ is not surprising; the salient feature of the BCS theory is that for spin independent phenomena such as ultrasonic attenuation, this effect does not occur since the matrix element for the transition becomes smaller and cancels the density of states effect, while for relaxation due to the contact interaction the effect is present. Strictly speaking, according to the BCS theory $1/T_1 \to \infty$ at $T = T_c$ since density of states $\rho(E_F)$ is finite, but $\int [\rho(E)]^2 dE$ diverges; since the BCS theory is only an approximation, and the excitation in reality have a finite lifetime, $1/T_1$ does not become infinite. Hebel and Slichter4 incorporated this lifetime effect by empirical smearing of the density of states function.

It is necessary to note that in the first works on NMR in superconductors long nuclear relaxation time allowed to overcome the main difficulty for the observation of the resonance caused by the Meissner effect using the method of cycling of dc magnetic field.5 Formation of nonequilibrium response of the nuclear spin system was performed in the superconductor state and the resonance signal was observed in the normal state. Because of a short relaxation time this method can not be used in the case of EPR. For a long time the possibility of using EPR of conduction electrons for the study of the superconducting state was considered to be impossible since the Cooper pairs which are formed by two electrons with opposite spins in the superconducting state have the zero total spin. Furthermore, superconductors expel completely the external magnetic field from their inside due to the Meissner effect. This makes impossible even the observation of the resonance of a localized moment which can be specially introduced into the superconducting matrices as a special spin probe. However, in type II superconductors in the mixed state magnetic field penetrates as the Abrikosov vortices.6 This offered a possibility to use EPR for the study of the type II superconductors.

The works concerning the study of superconductors by EPR were started more than 40 years ago when its pioneering observation by the group of E. G. Kharakhsh’yan7 was done at the Kazan Physical Technical Institute of the Russian Academy of Sciences (in present Zavoisky Physical Technical Institute). Soon after that two groups possessing the most sensitive in the world EPR equipment which allow to perform measurements at low and ultralow temperatures, join in the study of EPR in superconductors. These are the group of R. Orbach in California University and the group of K. Baberschke in Frei University in Berlin. The above groups have published a whole series of papers on the
EPR study of Gd$^{3+}$ ion in both the normal and superconducting state of different intermetallic compounds. The detailed analysis of the temperature dependencies of the linewidth and g-value performed in these works allowed to get information concerning the behavior of the electron magnetic susceptibility of a superconductor and the peculiarities of its electronic structure. These studies have been performed using the samples containing a small amount of magnetic impurity in order to exclude the broadening of the resonance line due to the spin-spin interaction. In principle, this information could be obtained using the NMR experiments.

As to the conduction electron spin resonance (CESR) even in the Abrikosov state due to the fast decrease of the elementary excitations above the superconducting gap upon lowering the temperature and large value of the spin-orbit interaction the possibility for observation of CESR remained open for many years.

CESR was observed at the later stage by Yafet et al. They reported the first observation of CESR in both the normal and superconducting state of pure niobium. The resonance displayed a g-value of 1.84±0.01 in both states. The linewidth narrows considerably in the superconducting state. The authors showed that this narrowing is a consequence of the coherence effects.

The influence of paramagnetic impurities on the properties of superconductors was one of the intensively investigated problems of superconductivity physics in 1970ies. The observation of EPR of a localized moment in type II superconductor added the EPR method to the number of physical methods used to study this problem. Being a direct detector of the formation of an electronic localized magnetic state, this method yields information on a number of important properties of a superconductor doped with a magnetic impurity. All the possible applications of EPR to superconductors have not yet been clarified completely, but the following can already be noted at present. The EPR method makes it possible to measure directly the exchange interaction of conduction electrons and the localized states, to obtain detailed information on the spin scattering of the conduction electrons individually for a given kind of impurity, to investigate the collective spin-density oscillations produced at sufficiently high concentrations of the paramagnetic impurity (the "electron bottleneck" effect) (see also APPENDIX II). Finally, and apparently most significantly, EPR makes it possible to investigate directly the character and the strength of the interactions between the electronic localized states in the superconducting phase and consequently to investigate the problem of the coexistence of magnetic order and superconductivity.

This paper presents the results obtained by the group of E. G. Kharakshyev concerning the first observation of EPR in type II superconductor, observation of new type of an exchange interaction between localized moments, magnetic ordering of impurities in the superconducting state and, finally, the phase separation in high-$T_c$ superconductors.

All EPR measurements were performed using an X-band spectrometer equipped by the home-made helium cryostat ($T=1.7±4.2$ K) and by the flowing helium gas system ($T=5±300$ K). First observation of EPR was done using spectrometer RE-1306 (Russia) and all other measurements using EPR spectrometer B-ER 418$^*$ (Bruker).

II. FIRST OBSERVATION OF EPR IN TYPE II SUPERCONDUCTOR

In this section we show that the observation of EPR of an electron localized moment in a type II superconductor in its vortex state is possible in principal. In contrast to NMR, for a long time the EPR in superconductors was failed to be observed. Besides the general difficulties in the observation of magnetic resonance because of the Meissner effect and expected strong inhomogeneous broadening of the line a short spin relaxation time appears to be an additional barrier for the observation of the EPR. Even under favorable conditions they do not exceed $10^{-8}$ s ($\sim 30$ Oe). These short relaxation times consequently entirely exclude the possibility for using the pulse measurements and the method of adiabatic cycling of magnetic field which was successfully used in NMR. Another method which allows to overcome the consequences of the Meissner effect and spacial inhomogeneity of magnetic field is the milling of the samples down to the sizes comparable with the superconducting penetration depth $\lambda$. However, in the case of EPR this method is noneffective since the preparation of a homogeneous ensemble of particles with the 100 Å sizes and defined magnetic impurity concentration represents an exceptionally complex technological task even for single-component superconductors. (Here we discuss the preparation of samples for the observation of EPR of the localized magnetic states.) For more complex multicomponent systems these difficulties increase. Finally, the existence of magnetic impurities suppresses superconductivity and decreases the critical parameters of superconductor. The most heavily this effect concerns the transition elements and weaker rare-earth elements. For the first observation of EPR in a superconductor it was natural to choose as an object of research a "bulk" (with dimensions $d>\lambda$) type II superconductor doped by rare-earth impurity. At the beginning we supposed that the search for the resonance signal should be performed in the vortex state, when the magnetic field partially penetrates into the sample and at the magnetic field close to the upper critical field $H_{c2}$ in order to decrease the effect of inhomogeneous broadening of the resonance line. Later on we obtained that in order to observe the resonance line on the background of baseline drift in a superconductor we should not be too close to the superconducting critical field.

The first attempts to observe EPR of a localized moment have been undertaken by us in the period from 1969 to 1971 for the metallic lanthanum samples doped
by the gadolinium impurity. From one side a metallic lanthanum doped by rare earth magnetic impurity is a very convenient matrix for the EPR study of rare-earth ions due to their good solubility and possessing of tempered chemical activity. Unfortunately, from another side it can be hardly obtained in a single-phase. It is well known that the pure metallic lanthanum crystallizes in two structural modifications: hcp with the double axis (α-La) and fcc (β-La). Both these modifications are superconducting with the superconducting transition temperatures $T_c$=4.9 and 6.0 K, correspondingly. Lanthanum demonstrates all properties inherent in type II superconductivity. Our measurements of the upper critical field for β-La yield $dH_{c2}/dT \approx 1.3$ kOe/K at $T_c \approx 6$ K. In principle, at $T \approx 2$ K we should have $H_{c2} \approx 5$ kOe. This means that at $T=2$ K the resonance field $H_0 \approx 3350$ Oe will be smaller than $H_{c2}$ and we should be able to observe EPR of our samples in the superconducting state. It is necessary to note that such favorable situation should occur for pure La samples. Doping the samples by Gd will decrease $T_c$. Our studies show that the $T_c$-suppression by 1 at.% of Gd $dT_c/dc \approx 4$ K/at.%.

Nevertheless, we decided to perform the first measurements using the dilute alloys of gadolinium in lanthanum. Altogether five samples $La_{1-x}Gd_x$ with $x = 5 \cdot 10^{-4} \div 5 \cdot 10^{-3}$ have been studied. The samples were prepared by melting the constituents under helium in a conventional induction furnace with subsequent quenching in the cold helium stream after switching off the furnace. As x-ray analysis has shown the quenching procedure allows to prepare the samples with predominant content of the cubic β-phase.

The EPR measurements were performed at the temperature range between 2 and 4.2 K. At all temperatures we observed a strong drift (almost vertical) of the baseline of spectrometer which is caused by the nonlinear field dependence of the surface impedance of a superconductor. (EPR spectrometer records the first derivative of the absorbed power on the dc magnetic field). In addition noises arising due to the vortex motion when sweeping the dc magnetic field further hamper the observation of the resonance. No resonance signal was detected in such background. Thus, our first attempt failed. Our analysis showed that the reason for this negative result was too small value of $H_{c2}$ for the studied samples which only slightly exceeds the resonance field. It was not enough to reach the acceptable conditions for observation of EPR on the background of the drift of the baseline. We also definitely observed that the values of $H_{c2}$ determined from the drop in curve of the surface impedance at $10^{10}$ Hz using the EPR spectrometer are noticeably smaller than the values obtained using constant current. This drop occurs at the dc magnetic field corresponding to equality of the microwave field energy and the superconducting energy gap. At small (compare to $H_{c2}$) magnetic fields the microwave energy is much smaller than the superconducting energy gap and the upper critical field determined from the drop of the surface impedance coincides with the value determined from the changing of the electrical resistivity using direct current. At the same time with increasing the dc magnetic field the superconducting gap decreases and the superconducting transition detected via the microwave surface impedance occurs at smaller magnetic fields.

On the next step of our search we decided to repeat our attempt using a superconductor with much higher critical parameters. That is the $La_3$In intermetallic compound doped by gadolinium impurity. Pure $La_3$In has $T_c=9.1$ K and $H_{c2} \approx 70$ kOe.

For our preliminary measurements we used the sample $La_{2.99}Gd_{0.01}In$ sample which was prepared by melting the constituents in the tantalum crucibles under pure helium in a conventional induction furnace. The sample for the measurements was cut in a plate shape with dimensions 10x4x0.5 mm. The $T_c$-value for our sample was of the order of 6 K. According to the data by Crow et al. this allowed us to conclude that the resonance field value $H_0$ lies well below the upper critical field $H_{c2}$ and the observed EPR signal (Fig. 1) comes from the superconducting state of sample. In reality an EPR signal was observed on the background of the field-dependent baseline which was approximated by the straight line and subtracted from the observed plot. EPR signal for our sample was recorded together with the signal of the small amount of the free radical DPPH (diphenylpicrylhydrazyl) which was placed into the working cavity at room temperature as a field label. As it is seen from Fig. 1, the resonance signal has a typical asymmetric ”metallic” shape and consists of the mixture of the dispersion and absorption curves. The pick-to-pick linewidth $\delta H = 280 \pm 20$ Oe and $g = 2.005 \pm 0.05$. It is interesting to note that the $\delta H$ and $g$-values are almost equal to the same values for $La_{1-x}Gd_x$ at corresponding concentration of gadolinium at $T=4.2$ K in the normal state. Thus, in this Section the possibility of observation of EPR in type II superconductor was demonstrated. The continuation of this study is presented in Section V.
III. NEW TYPE OF EXCHANGE INTERACTION

Both in the first and in the subsequent papers on EPR of a localized moment in superconductors, the investigations were carried out on intermetallic compounds with small amount of the gadolinium impurity. The choice of intermetallic compounds for the investigations in was determined by the need to have relatively high critical parameters for the samples doped with paramagnetic impurities. In the investigations of such samples by the EPR method, however, there is always the danger of the appearance of parasitic signals, which mask the true effect. This may be caused either by the tendency to oxidize of these compounds, or by the difficulty of attaining the necessary homogeneity and stoichiometry. It is therefore of interest to carry out the EPR investigations on paramagnetic impurities in a single-component type II superconductor. In this respect, metallic lanthanum is very attractive, in view of the good solubilities of rare-earth metals in it. The critical parameters of pure single-component superconductors are usually lower than the corresponding values for compounds. We met this situation when trying to observe EPR of Gd$^{3+}$ ion in lanthanum and failed (see Section II). Fortunately, this difficulty can be overcome choosing a paramagnetic impurity with a large g-value, for example, Erbium with g ≃ 6.8 corresponding to the resonance line field of 1000 Oe. In addition Erbium suppresses the superconductivity of the lanthanum much less than gadolinium. Our measurements show that $T_c$-suppression by erbium $dT_c/dc$ ≃ 0.4 K/at.%. Thus, the measurements can be performed up to high concentrations of the paramagnetic impurities, when the interaction between them becomes substantial. As it was mentioned in Section II metallic lanthanum crystallizes as a mixture of two modifications with hexagonal ($\alpha$-La) and face-centered cubic ($\beta$-La) lattices. However, the choice of erbium as the paramagnetic impurity makes it possible to disregard the presence of the hexagonal phase of the lanthanum, since the strong anisotropy of the g-value of the Er$^{3+}$ ion in a hexagonal crystal makes the EPR signal unobservable in the $\alpha$-phase in a polycrystalline sample.

We present here the results of investigations of EPR of the erbium localized moments in metallic lanthanum with relatively high concentrations of the magnetic impurity. These results have been published in 14–16.

A. EPR measurements. Experimental results

Besides the usual limit imposed on the real sensitivity of the EPR spectrometer for a metal as a result of the skin effect, in the superconducting state it is necessary to take into account also the increased noise due to the motion of the vortices and a strong dependence of the surface impedance of the superconductor when sweeping the dc magnetic field. The latter circumstance is partic-ularly significant near the transition temperature, where the EPR measurements are very difficult. The minimum erbium concentration that could be observed in the superconducting state was 0.5 at.%. The maximum concentration was 6 at.%. 1) Line shape. The EPR line shape in the normal state had the asymmetric shape usually observed for the bulk metallic samples and was well described by a superposition of Lorentzian dispersion and absorption curves. The linewidth (halfwidth of the absorption line at the $1/2$ amplitude) $\Delta H$ and the g-value were determined using the standard procedure. Figures 2 and 3 show a plot of the derivative of the resonant-absorption power of a sample in the superconducting state. Fig. 2 shows the background of the EPR signal at the temperature well below $T_c$ at the resonance field. The line shape, especially for small erbium concentrations (Fig. 3), differs substantially from a pure Lorentzian, principally as a result of the inhomogeneous distribution of the magnetic field inside the sample, caused by the appearance of the vortices. The shape of the resonance signal in the superconducting phase with allowance for the vortex lattice is given in APPENDIX I. As seen from Fig. 3, the calculated curve describes well the experimental spectrum. By reconciling the theoretical curves with the experimental data it is possible to obtain the true linewidth $\Delta H$ and the difference between the maximum $H_c$, and the minimum $H_{c1}$ fields in a sample that is in the mixed state at $H_{c1} \leq H \leq H_{c2}$.

![FIG. 2: Plot of the EPR signal in the superconducting state.](image-url)

![FIG. 3: EPR signal in the superconducting state. The points were calculated taking into account the vortex lattice with $\Delta H=35$ Oe and $H_c=84$ Oe.](image-url)
2) The g-value. In the normal state, the g-value was equal to 6.80±0.05. The proximity of the observed value of the g-value to the theoretical one for the doublet $\Gamma_7$, (for which $g = 6.77$ in a cubic field when account is taken of the intermediate coupling) is evidence that the ground state in our case is the doublet $\Gamma_7$, as follows also from our susceptibility measurements. This is an unequivocal confirmation of the fact that the resonance signal is due to the cubic $\beta$-phase of the lanthanum.

For the superconducting phase, when calculating the line shape by the scheme described in APPENDIX I, it was assumed that the magnetic field at the center of the vortex is equal to the external magnetic field. Actually, as shown, for example, by NMR measurements of single-crystal niobium samples of high quality, this field can noticeably exceed the external field. Therefore the values of the g-value, calculated from the spectrum distorted by the vortex lattice, may differ from the true values. For this reason, we do not analyze here the g-value in the superconducting region.

3) Temperature and concentration dependence of the linewidth. Figure 4 shows the dependence $\Delta H(T)$ for several samples in the studied temperature range, while Fig. 5 shows in greater detail the low temperature part of this dependence for one of the samples. Fig. 6 shows the concentration dependence of $\Delta H$ in the normal and superconducting states for all studied samples. These figures allow us to conclude the following: a) at temperatures below 14 K in the normal state, the temperature dependence of the linewidth can be roughly approximated by the linear relation $\Delta H = a + bT$; b) above 14 K, the temperature dependence of $\Delta H$ is no longer linear; c) the coefficients $a$ and $b$ depend on the concentration; d) upon transition into the superconducting state, the linewidth decreases sharply, and the jump is proportional to the erbium concentration; e) $\Delta H$ is constant in the superconducting state.

B. Discussion of results

1) Normal state. That part of the EPR linewidth which depends linearly on the temperature is due to thermal fluctuations of the exchange interaction of the localized $f$ electrons with the conduction electrons (the Korringa mechanism). If we introduce for the doublet $\Gamma_7$, which is ground state of Er$^{3+}$ in fcc La, an effective spin $S = 1/2$, then the Hamiltonian of the exchange interaction can be written in the form $g(g_L - 1)JSs/g_L$ ($s$ is the spin of the conduction electrons), and the exchange integral $J_{sf}$ is determined from the temperature slope of the linewidth $b$ (see APPENDIX II). As seen from Eq.(6), the measured quantity is the product of the exchange integral by the density of states. If we use for the electron density of state at the Fermi level the value $\rho(E_F) = 2$ eV$^{-1}$atom$^{-1}$spin$^{-1}$ known from measurements of the heat capacity then in the case of the sample with the smallest erbium concentration, when the effect due to the collective oscillations of the spin density of the localized moments and conduction electrons are each significant, we obtain from Eq.(8) the value $J_{sf} = 0.13$ eV.
It is of interest to compare this quantity with the data obtained from the dependence of $T_c$, on the concentration of the paramagnetic impurity. The presented EPR and susceptibility results show that at temperatures of the order of $T_c$, we can neglect the scattering of the electrons by the excited levels of erbium (see below). To obtain $J_{sf}$ in the presence of the crystal-field effects we can therefore use the formula of Abrikosov and Gor'kov\(^\text{20}\) (see APPENDIX II), which we express in terms of the effective spin. This yields a value $J_{sf} = 0.04$ eV, which differs noticeably from the corresponding value obtained from EPR. The observed discrepancy can be connected with the fact that in lanthanum the conduction electrons belong mainly to the s and d bands, and the contributions from these bands to the spin relaxation rate (the Korringa and Overhauser relaxations) and to the heat capacity may not be fully equivalent.

The proximity of the excited level to the ground level causes the temperature dependence of the linewidth to deviate from linearity at temperatures on the order of 14 K, as a result of the relaxation process of the Orbach-Aminov type\(^\text{21}\). Allowance for this mechanism leads to the temperature dependencies of the linewidth, shown by the solid lines in Fig. 4. It is interesting to note that all three set of crystal field parameters obtained in the calculation of the magnetic susceptibility make the same contribution to the relaxation.

The part $a$ of the EPR linewidth which does not depend on temperature, can be ascribed to magnetic dipole-dipole interactions. A contribution to the linewidth can also be caused by the distortion of the spatial distribution of the charge density of the conduction electrons, due to lattice defects. They lead to the appearance of a low-symmetry contribution to the crystal field and cause the g-value to be shifted as a result of mixing of excited states with the wave functions of the doublet $\Gamma_7$. It is important to emphasize here that whereas the scatter of the g-value is due to the mutual influence of the paramagnetic impurities, the linewidth will increase with increasing concentration, just as in the dipole-dipole broadening mechanism. On the other hand, the mutual distortion of the spin density of the conduction electrons by paramagnetic impurities leads to the known indirect RKKY exchange\(^\text{22}\), which suppresses the indicated two-particle mechanisms of EPR line broadening. The value of the RKKY exchange integral can be easily estimated in the free-electron approximation (see, e.g.\(^\text{22}\)): 

$$J_{\text{RKKY}} = \frac{9\pi Z^2 J^2_{sf}}{2E_f} \phi(k_f R), \quad \phi = \sin x - x \cos x \frac{x}{x^2},$$  \hspace{1cm} (1) 

where $Z$ is the number of conduction electrons per atom, $E_f$ is the Fermi energy, and $k_f$ is the corresponding wave vector. To this end it is necessary to calculate the value of the exchange integral $J_{sf}$, using the density of states of the conduction electrons $\rho(E_f) = 0.33$ ev$^{-1}$atom$^{-1}$spin$^{-1}$ calculated in the free-electron model for lanthanum. From the EPR data we obtain $J_{sf} = 0.08$ eV, and from the dependence of $T_c$ on the erbium concentration we get $J_{sf} = 0.1$ eV. The values of $J_{sf}$ are in fair agreement. The use of $J_{sf} = 0.08$ eV yields for the nearest neighbors in the lattice the value $J_{\text{RKKY}} = 2$ K, which is much higher than the energy of the magnetic dipole-dipole interaction (for which in our case the estimate yields - 0.05 K). This means that an exchange narrowing of the EPR line takes place.

2) Superconducting state. Upon transition to the superconducting phase, an additional reason for the broadening of the EPR line appears, because of the inhomogeneous distribution of the magnetic field in the sample at $H_{cl} < H < H_{c2}$. The experimental observed deviation of the shape of the EPR line from Lorentzian in the phase transition agrees with the assumption that a vortex structure is realized in our samples. The theoretical EPR line shape can be calculated by introducing the distribution function of the magnetic field in the superconductor (see APPENDIX I). The value $H_{c1} - H_{c2} = 70$ Oe obtained by this method for a sample containing 0.5 at. % Er (see Fig. 3) can be compared with the result obtained from measurements of the magnetic moment $M$ of the superconductor. For a triangular vortex lattice we have $H_{c1} - H_{c2} = -1.46 \cdot 4\pi M$\(^\text{23}\) which in our case yields 75 Oe, in good agreement with the value given above.

The most interesting feature of the results of the measurements in the superconducting phase is the sharp narrowing of the resonance line just below the superconducting transition temperature $T_c$. This observation was in contradiction to the commonly accepted point of view that the resonance line should broaden upon transition to the superconducting state. Let us consider the possible reasons for this effect. As a result of the appearance of coherence effects in the scattering of the conduction electrons the Köringa relaxation rate\(^\text{23}\) increases sharply near $T_c$ similar to the case of the NMR relaxation.\(^\text{23}\) At the same time, according to Mak\(^\text{24}\) the rate of exchange scattering of the conduction electrons $\delta_{ex}$ below $T_c$ (the Overhauser relaxation) also increases, and the spin-orbit scattering (the spin-lattice relaxation of the conduction electrons) decreases sharply. This circumstance enhances the conditions of the "electron bottleneck," and leads to a narrowing of the EPR line. This effect, however, can explain only in part the observed narrowing of the line, since the change of $\Delta H$ at high impurity concentrations exceeds the contribution due to the Köringa mechanism which can be obtained by the linear extrapolation of the $\Delta H(T)$ from $T_c$ to zero temperature.

Let us consider also another possible reason for increase of the exchange narrowing of the EPR line in the superconductor. The change of the RKKY exchange interaction upon transition into the superconducting state is determined by the correlations of the conduction electrons with opposite spin orientations, as a result of which the average spin susceptibility tends to zero. The local spin polarization of the electrons near the paramagnetic impurity is then canceled out as a result of the indicated correlations over much larger distances, on the order of the coherence length\(^\text{24}\). The corresponding change of the
The exchange integral is
\[
\Delta J_{RKKY} = \frac{9\pi^2 Z^2 J^2_f}{E_f^2(k_f R)^2} k_b T \sum_o \frac{\Delta^2}{\Delta^2 + \omega^2} \sin^2(k_f R) \times
\]
\[
\times \exp \left( \frac{2\Delta^2 + \omega^2}{\omega v_f} R \right), \tag{2}
\]
where \(h\omega = \pi k_B T(2n + 1)\), \(\Delta\) is the order parameter in the superconductor, and \(v_f\) is the Fermi velocity on the conduction electrons.

An estimate of this contribution by the method of moments shows that the change of the exchange narrowing of the EPR line is small, since the rate of reorientation of the localized spins depends on \(J_{RKKY}^2\). It must be noted, however, that the exchange field of spins of one orientation on a paramagnetic ion in a superconductor, at low impurity concentration, can greatly exceed the corresponding value for the normal metal as a result of the long-range action. We note in conclusion that the taking into account properly both mechanisms mentioned above, we can explain fully the observed discontinuity of the linewidth.

Thus, to interpret the EPR line narrowing effect one should suggest the enhancement the conditions for the "electron bottleneck" and approved theoretically the existence of the new type of the long-ranged exchange interaction between localized paramagnetic ions in the superconducting state. That is a kind of "super exchange" interaction between localized ions, the Cooper pair assisted (mediated) interaction over the distance of hundreds, even thousands angstroms.

IV. MAGNETIC ORDERING IN THE SUPERCONDUCTING STATE

In the previous Section it was shown that EPR provides a most effective method for investigating the nature and strength of the spin-spin interactions between localized electronic states in the superconducting phase. It accordingly becomes possible to use the EPR method to investigate one of the most controversial problems in the physics of superconductors - that of the coexistence of magnetic order and superconductivity. A large amount of papers on the experimental study of this problem using various physical methods have been published (see, e.g., the reviews by Maple and Roth).

In the work reported in this Section we used the EPR method for the first time to investigate the effect of magnetic ordering of impurities in a superconductor. The superconducting compound La\(_3\)In doped with Gd was chosen as the material for the investigation. Just for this system we have observed EPR of a localized moment in superconductor for the first time.

For all the investigated samples in the normal state, the shape of the EPR line of gadolinium localized states had the asymmetric shape usual for bulk metallic samples. The g-value and the linewidth \(\Delta H\) were determined using the standard technique. The width of the EPR line in the superconducting state was determined taking into account the vortex lattice (see APPENDIX I). The results of the measurements of the resonance linewidth for the investigated specimens are presented in Figs. 7 and 8.

The normal state. The temperature dependence of the
The experimental value $dT$ in atomic percent. That the temperature slope $b$ of the linewidth depends on the Gd concentration indicates that the conditions for an electron bottleneck in the relaxation of localized moments are satisfied (see APPENDIX II). In this case one can determine important spin dynamic characteristics of the conduction electrons from EPR data. From the temperature slope of the EPR linewidth using the value $\rho(E_F) = 1.7 \text{ eV} \cdot \text{atom}^{-1} \cdot \text{spin}^{-1}$ which we determined from the $dH_e/dT$ data with the aid of the Gor’kov relation, we obtain $\delta_{ei} = (8 \times 10^{10}) \text{c sec}^{-1}$, $\delta_{ei} = (1.7 \times 10^{13}) \text{c sec}^{-1}$, and $J_s = 0.01 \text{ eV}$, where $c$ is the gadolinium concentration in atomic percent.

One can also evaluate $\delta_{ei}$ from the dependence of the critical temperature of the superconductor on the magnetic-impurity concentration, using the well-known formula of Abrikosov and Gor’kov (APPENDIX II). The experimental value $dT_e/dc = 3 \text{ K}$ yields $\delta_{ei} = (6.7 \times 10^{13}) \text{c sec}^{-1}$. The difference between the values obtained for the exchange scattering rate from the EPR data and from the $dT_e/dc$ data is evidently to be attributed to the possibility that nonmagnetic scattering of conduction electrons by gadolinium impurities may contribute appreciably to the suppression of the superconductivity. In that case the estimate of the exchange-scattering rate based on the concentration dependence of the superconducting transition temperature would be overestimated. Further, the possibility cannot be entirely ruled out that the relaxation of localized gadolinium moments in $\text{La}_3\text{In}$ and the superconductivity of that compound may be due to electrons of different bands. Moreover, it must be borne in mind that the electron bottleneck effect arises only when the relaxation of localized moments is due to $s$-band electrons, since $d$ electrons have very short spin relaxation times.

The "residual" linewidth $a$ in the metal is determined by the spin-spin interactions and the fine structure. Estimates show that even in the absence of exchange narrowing, the contribution of dipole-dipole interactions to the linewidth does not exceed 100 Oe at the concentrations used in the present work. For the investigated samples, therefore, the linewidth is evidently determined mainly by the fine structure of the $\text{Gd}^{3+}$ ion and the inhomogeneities of the crystal, whose contributions are partially averaged by spin fluctuations induced by indirect exchange interactions.

As the temperature approaches the magnetic ordering point the correlation range increases sharply under the action of the exchange potential, and this leads to a corresponding increase in the linewidth and to a shift of the resonance toward the weaker magnetic fields. In the normal state, this effect is most clearly seen in the sample containing the 1.25-at.\% Gd concentration (Fig. 8).

On the basis of all the experimental data (part of them are not presented here), we can sketch the following qualitative picture of the magnetic state of the impurities in the investigated compound. At temperatures $T \leq 15 \text{ K}$ strong antiferromagnetic correlations between the neighboring spins were found from the magnetic susceptibility data. As the temperature decreases further, the weak exchange interactions, preferentially of ferromagnetic type at distances $R \leq 3 \text{ Å}$, lead to "freezing" of the spin system with the formation of a complex magnetic structure with a small spontaneous moment.

It should be noted that the intensity of EPR signal deviating only slightly from the Curie-Weiss law at low temperatures evidently give us reason to assume that the impurity was uniformly distributed in our specimens.

**The superconducting state.** The samples with gadolinium concentrations of 0.125, 0.25, and 0.75 at.\% become superconducting at temperatures in the range $6 \div 8 \text{ K}$, the EPR linewidth first increasing and then rapidly decreasing (Fig. 7). This behavior of the linewidth is similar to the change in the nuclear relaxation rate in a superconductor and is associated with the appearance of a gap in the elementary excitation spectrum. As the temperature decreases below 3 K the linewidth for the sample with the 0.125-at.\% Gd concentration does not change further, while those for the samples with the 0.25- and 0.75-at.\% Gd concentrations increase again.

As was noted above, for samples with low concentration of magnetic impurity at low temperatures the contribution from antiferromagnetic pairs to the spin-fluctuation frequency freezes out. It is therefore natural to assume that the observed behavior of the linewidth for the samples with Gd concentrations of 0.25 and 0.75 at.\% at temperatures below 3 K is due to this effect.

In investigating the coexistence of magnetic order and superconductivity it is important to answer the following question: Do superconductivity and magnetic order coexist in the same volume, or are the superconductive and magnetic phases spatially separated? Since the basis for the conclusion that the gadolinium impurities are magnetically ordered in the superconducting phase is the characteristic behavior of the resonance line near the magnetic ordering point, it is necessary to analyze the possibility that a parasitic signal from extraneous inclusions in the normal state may be superimposed on the EPR spectrum. The normal phase might be produced either by a nonuniform distribution of the impurity throughout the specimen or as a result of precipitation of a nonsuperconducting modification of the investigated compound.

The degree of spatial uniformity of the impurity distribution can be estimated from measurements of $T_c$ performed by the ac-susceptibility method. This method provides information on the variance of $T_c$ throughout the volume of the specimen, whereas measurements of $T_c$ based on conductivity methods do not, since in principle it is possible that normal-state inclusions may be shorted out by superconducting regions having high critical temperatures. If it is assumed that the fluctuation of the Gd concentration in the sample is the main reason for the broadening of the superconducting transition, the
temperature dependencies obtained for the volume that has passed into the superconducting state can be very well described under the assumption that the impurity is distributed normally in the specimen with a quite small standard deviation—e.g., with a standard deviation of $\sigma_\tau = 0.08\%$ for a sample with $\sigma_\tau = 1.25$ at.\% (i.e., $1.05\% \leq c \leq 1.45\%$, throughout 98\% of the volume of the specimen). Moreover, the EPR and magnetic susceptibility data on the sample containing 3 at.\% of Gd indicate that the distribution of the Gd$^{3+}$ ions is uniform even on small scales of the order of the mean distance between impurity atoms. As regards the presence in the sample of extraneous modifications of the compound of lanthanum with indium, it follows from the results of metallographic and x-ray studies that such modifications amount to no more than 4\%. The presence of 4\% or less of the normal phase in the investigated samples cannot appreciably distort the observed temperature dependence of $\Delta H$ in the superconductor since, as the results of special measurements show, the parasitic signal would not be strong enough to compete with the intense signal from the principal superconducting phase. It should also be borne in mind that the intensity of the EPR signal decreases very little (by 10-20\%) at the superconducting transition point.

Thus, our experimental data permit us to say with some confidence that magnetic order and superconductivity coexist in a single phase at temperatures below 3 K in the samples containing gadolinium concentrations of 0.25 and 0.75 at.\%. Since it is reasonable to assume that the temperature at which the line begins to broaden is proportional to the true magnetic ordering point, we can assert that the conditions for the appearance of magnetic order at least do not become more stringent at the transition to the superconducting phase; this becomes evident on comparing the data presented in Figs. 7 and 8. This is not even surprising, since theoretical calculations on transition to the superconducting state, the indirect exchange interactions responsible for the magnetic order do not undergo any substantial changes at distances shorter than the coherence length, which, in the investigated samples, exceeds the average distance between localized spins.

Thus, the use of the EPR method in the present work has made it possible to detect the emergence of magnetic correlations between spins in the superconducting phase itself; the results provide grounds for concluding that in La$_3$In containing gadolinium impurities, a magnetically ordered phase develops in the superconducting state in practically the same way as it does in the normal state.

This result was in a contradiction with Ginzburg’s statement that superconductivity and ferromagnetism are inconsistent. Indeed superconductivity is the state in which pair of electrons with opposite oriented spins form the Cooper pairs while ferromagnetism is forming-up by the localized moments and polarized by them spins of conduction electrons in one direction: these two phenomena are antagonistic at any temperature. Observation of magnetic ordering in the superconducting state by group of Kharakhash’yan was evidence for the noncollinear magnetic ordering. It appeared that the magnetic and the superconducting orderings can coexist if the mutual tuning takes place.

V. PHASE SEPARATION IN 1:2:3 HIGH-$T_c$ SYSTEM

After the discovery of superconductivity above 30 K by Bednorz and Müller in the La-Ba-Cu-O system, investigations on the synthesis of new superconducting metal oxides were started. Soon after, superconductivity at temperatures above the nitrogen boiling point was discovered by Chu and collaborators in multi-phase samples of Y-Ba-Cu-O. Subsequently it has been established that the superconducting phase with $T_c=90$ K has the formula YBa$_2$Cu$_3$O$_{7-\delta}$. Among the several striking features of these new superconducting systems, now commonly named as 1:2:3-systems, their relation to magnetism is the most surprising. Indeed, in x-ray homogeneous single phase YBa$_2$Cu$_3$O$_{7-\delta}$, Curie-like temperature dependence of magnetic susceptibility has been observed above $T_c$. Moreover, the value of susceptibility varied over a wide range. Bearing in mind that superconductivity and magnetism are antagonistic phenomena, it is surprising that $T_c$ is unchanged when the Curie-like part of susceptibility is varied. The next interesting feature of these systems is their indifference to the magnetic state of rare-earth ion substituting for yttrium: $T_c$ over the rare-earth series is practically the same.

In this Section we report the results of our EPR studies of 1:2:3-system samples with the different oxygen content. Our results have been published in Refs. As a spin probe we used the Gd$^{3+}$ ion in $Y_{1-x}$Gd$_x$Ba$_2$Cu$_3$O$_{7-\delta}$.

A. Samples

To obtain the $Y_{1-x}$Gd$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ samples with small gadolinium content, the $Y_{1-x}$Gd$_x$ alloy was first prepared. Then it was dissolved in nitric acid, and the salt solution that was obtained was evaporated and decomposed at the temperatures of the order of 600° C. We believe that the Y$_{1-x}$Gd$_x$O$_3$ oxide obtained was sufficiently homogeneous and was used when synthesizing the samples. Changing the temperature of synthesis, the annealing time, the rate of cooling, and the partial oxygen pressure, we prepared the samples with a different degree of the orthorhombic distortion.

The oxygen deficiency in YBa$_2$Cu$_3$O$_{7-\delta}$ samples was determined using as a reference the correlation of the lattice parameters with the oxygen content. It was found that the minimum value of the oxygen deficiency for our samples corresponded to 0.15 and the maximum one to
$\delta = 0.5$. The oxygen concentration for the samples containing gadolinium was evaluated by the same way.

To increase the signal-to-noise ratio, EPR measurements were performed on powder samples prepared by grinding of pellets. The powder with particle dimensions of the order of the single crystallite sizes ($\sim 10 \mu m$ from optical microscopy) was mixed with paraffin and placed into a quartz ampule.

**B. Resistivity**

For the samples with small oxygen deficiency, the linear temperature dependence of the resistivity was observed above $T_c$. All the samples with metallic behavior showed a sharp ($\Delta T_c \leq 2 K$) transition from the normal to the superconducting state. When lowering the oxygen content the temperature slope of the resistivity became smaller. These samples had a broad transition to the superconducting state. For the samples with a large oxygen deficiency, semiconducting behavior of resistivity of the form $\rho(T) \sim \exp(A/T^\alpha)$ was observed. In particular for the samples with $\delta = 0.5$ the $A$- and $\alpha$-values were of the order of $10^2 K^{1/2}$ and 1/2, respectively.

**C. The EPR of Gd$^{3+}$ ions in Y$_{1-x}$Gd$_x$Ba$_2$Cu$_3$O$_{7-\delta}$**

The EPR measurements were performed at different temperatures in the range between 1.5 and 300 K. Fig. 9 shows the EPR signals for Y$_{0.99}$Gd$_{0.01}$Ba$_2$Cu$_3$O$_{7-\delta}$ samples with $\delta=0.15$ and 0.5. The observed fine structure of the EPR spectra is typical for powder samples with a small gadolinium content. The single-line spectrum of Gd$^{3+}$ ions was observed for the GdBa$_2$Cu$_3$O$_{7-\delta}$ samples with $\delta=0.15$ and 0.5 (see Fig. 10). For these samples the fine structure is narrowed by the exchange interaction between the gadolinium localized moments. Figure 11 shows the temperature dependence of the linewidth. In both samples, at temperatures above 90 K the linewidth increased with the temperature. For GdBa$_2$Cu$_3$O$_{7-\delta}$ sample near $T_c=83 K$ one can see a slight anomaly: broadening of the line immediately below $T_c$ and then rapid narrowing. This behavior of the linewidth is caused again by the appearance of the superconducting gap and of the superconducting coherence effects. When lowering the temperature below 50 K, the EPR signal begins to broaden and shift to the low-field region. This broadening of the EPR line is caused by magnetic ordering of Gd$^{3+}$ ions similar to the case discussed in Section IV.

**D. Heterogeneity of System**

The temperature behavior of the Gd$^{3+}$ ion’s EPR spectra for Y$_{1-x}$Gd$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ and GdBa$_2$Cu$_3$O$_{7-\delta}$ samples with different oxygen deficiency shows the Korringa-like behavior in the relaxation of gadolinium localized moments. For the samples with $\delta = 0.15$, it is not surprising because the temperature dependence of resistivity above $T_c$ has metallic character, but for the samples with $\delta = 0.5$, this result is unexpected. When we studied the temperature dependence of resistivity, we obtained the “semiconducting” behavior in the form $\rho(T) \sim \exp(A/T^\alpha)$. Observation of such law with $\alpha = 1/4$ for the 1:2:3-system with large oxygen deficiency led Mei at al. to conclusion that due to Anderson localization of current carriers in such samples, hopping conductivity with varying lengths takes place. Our data on EPR, however, rule out this possibility. The point is that
in the vicinity of Anderson transition, where resistivity increases with the lowering the temperature, localized moment’s relaxation rate has also to increase due to increasing of the correlation time of conduction electron’s spin fluctuations. We observed just the opposite effect: EPR linewidth (the localized moment’s relaxation) decreases with the lowering the temperature.

Another possibility to understand the metallic character of EPR and “semiconducting” behavior of resistivity for the samples with $\delta = 0.5$ is the supposition about the granularity of our samples. In granular system the tunneling between metallic particles occurs by the path where the combination of two factors – transfer integral $\exp (-d/r_0)$ and activation probability $\exp (-e^2/\varepsilon k_B T)$ – is most favorable when varying the distance $d$ between granules. Here $r_0$ is the radius of localization and $\varepsilon$ is the dielectric permeability of nonmetallic regions. As a result, for resistivity, one can obtain the law $\rho(T) \sim \exp(A/T^{1/2})$, with $A = (4e^2r_0\varepsilon k_B)^{1/2}$, which is close to the law observed in our experiments.

So the different behaviors of the resistivity and metallic character of EPR may be consistent with each other if one assumes that samples under study are heterogeneous and consist of metallic and dielectric phases.\(^{33,34}\)

One may think that for the sample with $\delta = 0.15$, there is percolation, while for $\delta = 0.5$ there is not. More unequivocal conclusions may be derived from the analysis of the EPR lineshape for the samples of GdBa\(_2\)Cu\(_3\)O\(_{7-\delta}\). The lineshape of the Gd\(^{3+}\) EPR signal (Fig. 10) shows a noticeable deviation from a Lorentzian, especially for the GdBa\(_2\)Cu\(_3\)O\(_{6.85}\) sample. We suppose that the observed EPR signal consists of two signals with nearly equal g values ($g \approx 1.99$) but with different linewidths. The best simulation of the observed EPR spectra for any temperatures see (Fig. 10) was obtained by summing up two Lorentz lines with the following linewidth values. For the first line, the linewidth linearly depends on the temperature in accordance with the $\Delta H = a + bT$ law, where $a = 580$ Oe and $b = 0.9$ Oe/K. For the second one, the linewidth does not depend on the temperature and is equal to 1000 Oe. We suppose that these signals are determined by metallic and dielectric components, respectively. The pronounced nonlinearity of the observed temperature dependence of $\Delta H$ in the normal state (Fig. 11) proves to be the result of interference of these two signals. Analysis shows that for the GdBa\(_2\)Cu\(_3\)O\(_{6.5}\) sample, the contributions from the dielectric and metallic regions to the EPR signal are equal. The lack of dispersion contribution to the EPR signal indicates that the thickness of the metallic regions in this sample is much smaller than the skin depth. That is why the fraction of metal may be estimated as 50%. For the GdBa\(_2\)Cu\(_3\)O\(_{6.85}\) sample, the integral intensity of the EPR signal was three times smaller than for the GdBa\(_2\)Cu\(_3\)O\(_{6.5}\) sample. Since the number of Gd\(^{3+}\) spins is equal for both samples, the loss of the signal intensity may be caused only by the skin effect. If the metal portion is designated by $y$ and the EPR signal intensity in the absence of the skin effect is assumed to be equal to one, then, for GdBa\(_2\)Cu\(_3\)O\(_{6.85}\), it may be written that $\beta y + (1 - y) = 1/3$ (here $\beta$ is the relative portion of metal which forms EPR signal). Taking into account that contribution of dielectric and metallic regions to the simulated spectrum relate to each other as $7:3$, it may be written that $(1 - y)/\beta y = 7/3$. From these two relations, $y = 0.77$ and $\beta = 0.13$ is found. Thus the metal portion in this sample may be estimated as 77%.

At the same time, for this sample there is a loss of about 87% of the metallic EPR signal intensity due to the skin effect. However, when simulating the EPR spectrum, it was necessary to admix -20% dispersion signal to absorption signal in contrast to the situation of bulk metallic samples, where the equal mixture of dispersion and absorption signals is as expected.\(^{36}\) This probably suggests that in the studied samples, metallic regions form a net in which no less than 10% of the metal volume has characteristic dimensions considerably smaller than the skin depth.

**E. Discussion**

Our data on EPR of Gd\(^{3+}\) ions give evidence that the samples studied with 1:2:3-structure are heterogeneous and consist of metallic and dielectric regions. The variation of the volume ratio of metallic and dielectric phases established in this study allows us to suppose that in metallic regions the oxygen deficiency $\delta$ is close to zero and in dielectric ones is close to 1. Proceeding from the above, many peculiarities of the 1:2:3-system may be understood. In particular, small critical current values, which are probably limited by availability of weak links between metallic regions, become clear. Different behavior of the resistivity with temperature which has been observed for samples with different oxygen content may be also comprehended in the framework of this paper.

Our data seem to be consistent with results ob-
tained by other methods. Thus electron microscopy investigations\textsuperscript{38} utilizing microdiffraction and selected area diffraction on isolated single-crystal grains of the orthorhombic phase of YBa$_2$Cu$_3$O$_{6−δ}$ revealed local variations in orthorhombic parameter $Δa/a = 2(b−a)/(b+a)$. It was found that the microscopic values of $Δa/a$ varied from zero to more than twice the macroscopic value when scanning the surface of the sample by an electron beam.

A pseudobinary phase diagram was proposed by Caponi \textit{et al.}\textsuperscript{38} based on the log $P_{O_2}−1/T$ plots, quenching investigations, and high-temperature x-ray diffraction analysis. Different regions of the phase diagram were proposed to correspond to the first orthorhombic phase ($O_1$), the second orthorhombic phase ($O_{11}$), the tetragonal phase $T$ and coexistence of two phases. In Ref.\textsuperscript{39} the electron micrograph study gave the possibility of discussing the mechanism for the $O_1 → O_{11} → T$ phase transformations caused by the removal of oxygen atoms from the samples. If one supposes that the tetragonal $T$ phase is a dielectric and the orthorhombic $O_1$ phase is a metal, then the paramagnetic regions forming the copper-EPR may be referred to the orthorhombic $O_{11}$ phase.

All of the results obtained in Refs.\textsuperscript{37–39} and in the present Section are consistent with the sample being in spinodal decomposition region as predicted by Khachatryan \textit{et al.}\textsuperscript{40,41}. They pointed out that the nonstoichiometric compound YBa$_2$Cu$_3$O$_{6−δ}$ is thermodynamically unstable at low temperature. They postulated that under ordinary cooling conditions, the phases have no time to reach equilibrium and thus constitute a spinodally decomposed sample with a microscopic distribution of oxygen vacancy ordering. Thus, the slight variations in preparation conditions may be the reason for different physical properties of the samples obtained.

In conclusion, the EPR method happened to be rather informative in studying unusual properties of high-$T_c$ superconductivity. In spite of high values of the superconducting transition temperature $T_c$ the critical current values which destroy superconductivity were not too much. The temperature behavior of the Gd\textsuperscript{3+} ions spectra for the samples with $δ=0.15$ and $0.5$ demonstrates the "metallic" character of the EPR while the electric resistivity for the sample the with $δ=0.5$ manifests the "semiconducting" behavior. These observations lead us to the supposition about granularity of samples. In granular system due to the tunneling of electrons between metallic particles resistivity reveals the "semiconductive" feature as it was observed in our experiments. So the different behaviors of the resistivity and metallic character of EPR for the samples with $δ=0.15$ and $0.5$ may be consistent with each other if one assumes that samples under study are heterogeneous and consist of metallic and dielectric components.

VI. CONCLUDING REMARKS

This historical review of the past EPR research on superconductors in Kazan would not be complete without making a link to the present time. In particular, early EPR experiments on the high temperature superconductor YBCO is worth to assess in the current perspective. These works have been performed soon after the advent of high-$T_c$ superconductivity (HTSC) and since then an enormous progress in the understanding of the normal state and superconducting properties of the cuprates has been achieved. With this accumulated knowledge that early conclusion on the intrinsic heterogeneity of YBCO gained from the EPR data would sound not really surprising. It is well established now that the physics of HTSC is driven by the interplay of spin, charge and lattice interactions which give rise to novel electronic and magnetic phases and may even be a cause of the HTSC (see, e.g., popular reviews\textsuperscript{42–45}). The entanglement and competition of different states manifest in such exotic phenomena as the "fractionalization" of an electron in terms of the separation of spin and charge and the emergence of stripe phases where magnetic insulating phase is separated by the (super)conducting phase on a nanoscale. But at the time of our EPR experiments these "revolutionary" concepts that contradicted the wisdom of conventional uncorrelated metals and superconductors have not even been proposed. In that sense we were very fortunate to obtain one of the first experimental evidences of the intrinsic multiphase character of YBCO where the simultaneous occurrence of magnetic and superconducting regions indeed turns out to be an inherent property of HTCS cuprates.

Experimental EPR works beginning from the mid of the 90-ths of the past century dedicated to a further exploration of an interplay of superconductivity and magnetism in the cuprates are nicely reviewed in the paper by B. Elschner and A. Loidl\textsuperscript{46}. The readers interested in more details are refereed to this article. Here, it is appropriate to mention a few of those works which have attracted that time a lot of interest in the condensed matter community. Introducing local EPR spin probes in superconducting cuprates turns out to be a fruitful approach. As an example, the group around A. Janossy has employed high-field EPR on Gd doped YBCO to study the properties of the evading pseudogap phase\textsuperscript{47,48}. The group around V. Kataev has focused on Gd-EPR studies of the antiferromagnetic dynamics in the stripe phase of (La,Eu)$_2$SrCuO$_4$\textsuperscript{49,50}. The group around B. Elschner has used alternatively Mn\textsuperscript{2+} ions as spin probes imbedded directly in the CuO$_2$ planes to study the spin correlations in La$_{2−x}$Sr$_x$CuO$_4$\textsuperscript{51}. This group has even reported an intrinsic EPR signal in La$_{2−x}$Sr$_x$CuO$_4$ which has been attributed to the formation of a three-spin polaron, consisting of two Cu\textsuperscript{2+} ions and one p hole\textsuperscript{52}. Besides cuprates, other "less correlated" superconductors have been addressed with EPR in the near past. Particularly remarkable was an observation of conduction
electron spin resonance in superconducting MgB$_2$. Finally, soon after the discovery of a new class of high temperature superconductors on the basis of iron pnictides in 2008, the EPR method has begun to make valuable contributions to the understanding of the physics of these novel materials. One can mention a number of recent interesting works addressing the normal and superconducting properties of iron arsenides by Eu-EPR in the so-called 122-family and by Gd-EPR in the 1111-family.

Other results of our study performed from 1972 to 1977 also should be mentioned. They are the following.

1. We found an experimental evidence for existence of the new type of the indirect exchange interaction between the localized moments through the electrons constituting the Cooper pairs.

This superconducting indirect exchange interaction has been predicted theoretically by Anderson and Suhl. The physical origin of this interaction is the following. In the normal state the main exchange between the rare-earth localized moments in metals is the Ruderman-Kittel-Kasuja-Yosida indirect exchange interaction via the conduction electrons. It means that the localized moment due to the $sf$-interaction polarizes the spin of conduction electron. This spin polarization oscillates in space with changing its sign. Spin of another localized moment via the same $sf$-interaction feels this polarization. The sum of this indirect exchange over the lattice gives a possibility to predict the type of magnetic ordering which would occur at low temperatures. At high concentrations of magnetic impurities the ferromagnetic or antiferromagnetic orders may occur. At small impurity content very often a spin glass state is realized. In the superconducting state the situation is rather different. As in the case of the normal state the spin of the localized moment polarizes the spin of electron. Another electron constituting the Cooper pair at the distance of the order of the superconducting coherence length $\xi$ (the Cooper pair size) due to the $sf$-exchange interaction polarizes the spin of another localized moment in opposite direction. Thus the range of the indirect exchange interaction increases from the mean-free path $l$ of conduction electrons ($\sim 20$ Å) in the normal state up to the superconducting coherence length $\xi$ (for the LaEr dilute alloys $l << \xi$) in the superconducting state. This new superconducting exchange due to its antiferromagnetic origin may lead to a new type of the magnetic ordering called by Anderson and Suhl as a cryptoferromagnetic state. In the limiting case it is a small-scale domain state with a period of the order of the coherence length.

2. We also proved that the superconductivity and magnetic ordering of impurity may coexist.

Now it is well established that in order to coexist superconductivity and ferromagnetism should mutually adjust to each other. For example, the complex study of some ternary borides (see, e.g., review by Buzdin and Bulaevskii and references therein) gave a possibility to conclude that at some temperature range cryptoferromagnetism is realized in the superconducting state. When lowering the temperature further, ferromagnetism arises and superconductivity disappears. To determine which state is preferable: the superconducting/cryptoferromagnetic or the normal/ferromagnetic, it is necessary to compare the free energies of these two possibilities.

More exciting examples of mutual tuning of superconductivity and ferromagnetism were found in the thin film heterostructures consisting of superconducting and ferromagnetic layers. In these systems the superconductivity and ferromagnetism are separated in space. The properties of the superconducting and the ferromagnetic layers and coupling between the layers can be controlled and changed independently. This opens the possibility to observe much more interesting phenomena than in alloys and intermetallic compounds. In particular, one of them is the evidence for arising the cryptoferromagnetism in the Pd$_{1-x}$Fe$_x$ layer at its small thicknesses in the S/F bilayer. This result was obtained in epitaxial V/Pd$_{1-x}$Fe$_x$ using the FMR technique. Another one, the so-called spin screening effect when the spin polarization of conduction electrons in the ferromagnetic layer leads to the polarization of electron spins in the superconducting layer with opposite sign at the distance of the order of the superconducting coherence length from the F/S interface, was found recently. The scale of this effect is the coherence length because it is also caused by the superconducting correlations.

The author is grateful to Dr. Vladislav Kataev for helpful discussion. Further we thank Dr. Aidar Validov for technical support in the spectra restoration.
APPENDIX I

EPR line shape in a superconductor

In the previous Section we present the experimental evidence for the possibility to observe EPR of a localized moment in the superconducting state. Surprisingly the observed linewidth did not exceed its value in the normal state. This means that in order to understand the reason for unchanged linewidth upon transition from the normal to the mixed superconducting state it is necessary to calculate line shape in the Abrikosov vortex state taking into account the magnetic field distribution. This mixed state is characterized by the presence of an ordered lattice of tubes of magnetic flux, or vortices, surrounded and maintained by superconducting currents. The magnetic field decreases from a maximum value at the center of an isolated vortex over a characteristic distance $\lambda$, the London penetration depth. The superconducting order parameter grows from zero at the center of the vortex over a distance of the order of $\xi(T)$, the coherence length, with $\xi(T) < \lambda(T)$. For applied fields far from both $H_{c1}$ and $H_{c2}$ (the lower and upper critical fields, respectively) the vortex density is not too great. Experiments by Redfield in this region confirmed the ordered arrangement of the vortices, and verified that the lattice symmetry was triangular.

The distribution of the probabilities of encountering a given magnetic field in a triangular vortex lattice can be approximated by the analytic function:

$$f(x) = \begin{cases} 
0.837 - 0.500 \ln(-x), & 0.08 < x < 0 \\
0.236 - 0.576 \ln x, & 0 < x < 0.92
\end{cases} \quad (3)$$

Here $x = (H - H_s)/(H_v - H_c)$, $H_v$ and $H_c$ are the maximum and minimum fields in the lattice, $H_s$ is the field at the saddle point of the unit cell of the vortex lattice. If the shape of the homogeneously broadened EPR line in metal is determined by the Lorentz line

$$I_{\text{norm}}(H) = \frac{1}{\pi} \frac{\Delta H + H}{(\Delta H)^2 + H^2} \quad (4)$$

where $\Delta H$ is the half-width of the line at half-height and $H$ is the magnetic field relative to the center, then the EPR line shape with allowance for the broadening due to the vortex lattice is determined by the convolution

$$I_{\text{sup}}(H) = \int I_{\text{norm}}(H_1 - H)f\left(\frac{H_1 - H_c}{H_v - H_c}\right) dH_1 \quad (5)$$

The observed behavior of the spectrum is qualitatively consistent with the absence of pronounced broadening in the superconducting state due to the vortex structure at certain values of parameters. The average internal field is smaller than in the normal state; that is, a part of the flux is excluded. Increasing the amplitude of the high-field wing of the resonance line is due to the discontinuity at the maximum field $H_v$. 

\[57\] A. Alfonsov, F. Muranyi, V. Kataev, G. Lang, N. Leps, L. Wang, R. Klingeler, A. Kondrat, C. Hess, S. Wurmehl, A. Koehler, G. Behr, S. Hampel, M. Deutschmann, S. Katrych, N.D. Zhigadlo, Z. Bukowski, J. Karpinski, B. Büchner, Phys. Rev. B 83, 94526 (2011).

\[58\] A. Alfonsov, F. Muranyi, N. Leps, R. Klingeler, A. Kondrat, C. Hess, S. Wurmehl, A. Koefiler, G. Behr, V. Kataev, B. Büchner, JETP 114, 662 (2012).

\[59\] A. I. Buzdin, L. N. Bulaevskii, Adv. Phys. 34, 175 (1985).

\[60\] I. A. Garifullin, D. A. Tikhonov, N. N. Garif’yanov, M. Z. Fattakhov, K. Theis-Bröhl, K. Westerholt, and H. Zabel, Appl. Magn. Reson. 22, 439 (2002).

\[61\] R. I. Salikhov, I. A. Garifullin, N. N. Garif’yanov, L. R. Tagirov, K. Theis-Bröhl, K. Westerholt, and H. Zabel, Phys. Rev. Lett. 102, 087003 (2009).

\[62\] R. I. Salikhov, N. N. Garif’yanov, I. A. Garifullin L. R. Tagirov, K. Westerholt and H. Zabel, Phys. Rev. B 80, 214523 (2009).

\[63\] Such calculations have been also performed by Orbach.

\[64\] R. Orbach, Phys. Lett. A 47, 281 (1974).
EPR linewidth is determined by the Korringa law

\[ \delta_{le} \]  

complies to the Korringa law \[ \delta_{le} \geq \delta_{el} \]. The bottleneck affects the position as well as the width of the resonance line. The thermal broadening of the EPR linewidth \[ \Delta \delta_{le} \] is reduced. This was first calculated by Hasegawa\textsuperscript{12}.

Assuming \( g_i \approx g_c \), the theory yields

\[ \delta_{le} = \frac{\delta_{el}}{\delta_{ci} + \delta_{el}} \delta_{Kor}^{\text{Kor}}, \quad b = \frac{\hbar}{g \mu_B} \left( \frac{\delta_{el}}{\delta_{ci} + \delta_{el}} \right) \delta_{Kor}^{\text{Kor}}. \]

Second, bottleneck regime \( \delta_{ei} \geq \delta_{el} \).

Very often for high concentration of impurity \( \delta_{ei} \) may be of the same order of magnitude as \( \delta_{el} \). Then the subsystem of the conduction electrons is not longer in thermal equilibrium with lattice. The effective relaxation rate \( \delta_{le} \) is reduced. This was first calculated by Hasegawa\textsuperscript{12}.

\[ \Delta g = \left( \frac{\delta_{el}}{\delta_{ci} + \delta_{el}} \right) \Delta g_{\text{max}}. \]

Thus \( \delta_{Kor}^{\text{Kor}} \) corresponds to the "Korringa rate" and \( \delta_{ei} \) to the "Overhauser rate" which can be also obtained from "detailed balance" to susceptibility of the two subsystems \( \chi_i / \chi_c = \delta_{ei} / \delta_{le} \). Thus

\[ \delta_{ei} = \frac{2\pi}{\hbar} \rho(E_f) J_{sf}^2 S(S + 1)c. \]

From another side, \( \delta_{ei} \), is the controlling parameter for pair-breaking in the superconducting state. The theory by Abrikosov-Gor'kov\textsuperscript{12} well describes the \( T_c \)-suppression by magnetic impurity.

\[ \ln(T_c / T_{c0}) = \psi \left( \frac{1}{2} \right) - \psi \left( \frac{1}{2} + 0.14 \frac{\alpha}{\alpha_{cr} T_c} \right). \]

The pair breaking parameter \( \alpha \) and its critical value \( \alpha_{cr} \), where superconductivity is completely destroyed, are given by the theory in the first Born approximation

\[ 4 \hbar \alpha_{cr} = k_B T_{c0} / \gamma; \]

\[ 4 \hbar \alpha_{cr} = c \rho(E_f) J_{sf}^2 S(S + 1). \]

This equation yields

\[ \left| \frac{dT_c}{dc} \right| = \frac{3\hbar \pi}{16 k_B} \frac{d\delta_{ei}}{dc}. \]

This means that

\[ \left| \frac{dT_c}{dc} \right| = -\frac{\pi^2}{8 k_B} c \rho(E_f) J_{sf}^2 S(S + 1). \]