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New Approach to the Formation of a Bose–Einstein Condensate

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Abstract
The observation of the exchange narrowing effect is a routine event in EPR spectroscopy. In this paper, I want to draw attention to the fact that every time we observe an exchange narrowing of the EPR spectrum, we have a gas of identical bosons, where the prerequisites of BEC formation are satisfied at room temperature. Imagine the possibility to create BEC without the need to cooling down to nano Kelvin temperatures to get a gas of identical bosons because the phenomenon of exchange narrowing of the EPR spectrum can be easily observed at room temperatures. This article provides a detailed explanation of how a gas of identical bosons can be formed at room temperature in dilute solutions of paramagnetic particles with a discrete EPR spectrum of individual particles. There are still many questions about the Bose–Einstein condensation of a spin polariton gas, which is created under conditions of exchange narrowing of EPR spectra. With the expectation of obtaining additional information about the condensation of bosons in the situation under consideration, this article proposes the protocol of one EPR experiment to prove that the effect of exchange narrowing of EPR spectra can be instrumental in creating BEC in dilute solutions at room temperature.

1 What Prerequisites must be Fulfilled in Order to Obtain a BEC?

The Bose–Einstein condensate (BEC) was suggested as a state of atoms at very low temperatures when a sufficiently large number of atoms are in the ground non-generate electronic state [1].

BEC is formed not only by atoms, but also by quasiparticles (collective excited states). Today, examples of the formation of BEC of quasiparticles (magnons) in magnetically ordered solids are known (see, e.g., [2, 3]). The formation of BEC of

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quasiparticles means that photons pump the excited collective states in the system, which are all in the same quantum state. As a result, the coherence of the quasiparticles state is manifested in the system on a macroscopic scale.

The BEC of quasiparticles has an important difference from the BEC of atoms in the ground state: unlike atoms in the ground state, quasiparticles have a finite lifetime, a system is not in thermodynamic equilibrium state. This circumstance reduces the stationary concentration of quasiparticles, and this may prevent the achievement of a concentration of quasiparticles sufficient for the formation of BEC. But quasiparticles also have an advantage, since it is possible to create an ensemble of identical quasiparticles (identical elementary excitations) even at room temperatures.

To form a BEC, quasiparticles must satisfy several prerequisites:

Prerequisite #1. There must be a mechanism for creating identical elementary excitations, i.e. a mechanism for creating identical quasiparticles.

Prerequisite #2. Quasiparticles must be bosons so that many identical quasiparticles can be in the same state.

Prerequisite #3. Those quasiparticles must be sufficiently long-lived.

Prerequisite #4. There must be a sufficiently high concentration of quasiparticles so that the gas of identical quasiparticles can turn into a condensate.

This article shows how the effect of exchange narrowing of EPR spectra allows to satisfy all these prerequisites.

2 Understanding the Exchange Narrowing of EPR Spectra Phenomena

Manifestations of spin exchange in the shape of the EPR spectra open a way to create and monitor spin quasiparticles of excited states in dilute solutions of free radicals.

2.1 Phenomenological Description of the Exchange Narrowing of EPR Spectra

Note that stable free radicals with one unpaired electron are indicated below as paramagnetic particles. This is because it is nitroxide radicals that are used in molecular biology and chemistry as spin probes to study molecular mobility, in particular, to find the frequency of bimolecular collisions in complex systems (biological media, porous structures, polymer solutions). For that reason, most EPR studies of spin exchange have been carried out in solutions of stable nitroxide radicals (see, e.g., [4–6]). It is for spin exchange in dilute solutions of radicals that experimental data have been obtained that directly confirm the formation of collective modes of motion of magnetization caused by the Heisenberg exchange interaction in the course of random bimolecular collisions of radicals (see, for example, [7–10]). By ‘dilute solution’, we mean that the number of solvent molecules greatly exceed the number of radicals, so that collisions involving three or more radicals can be ignored.

The possibility of obtaining BEC in dilute solutions of free radicals (paramagnetic particles) was highlighted during the formulation of the new paradigm of spin

exchange and its manifestation in the shape of EPR spectra [11–16]. It appeared that EPR spectroscopy can create an ensemble of quasiparticles in one definite quantum state and can monitor the state of this ensemble.

Spin exchange is a change in the spin state of the unpaired electrons of two radicals A and B in a random collision

$$A(\uparrow) + B(\downarrow) \rightleftarrows A(\downarrow) + B(\uparrow) \tag{1}$$

In Eq. (1), the arrows indicate the unpaired electron spin states of two radicals in a collision. The change in spin states is caused by the Heisenberg exchange interaction during bimolecular collisions

$$\mathbf{H}_{\text{ex}} = J(r)\mathbf{S}_{\text{A}}\mathbf{S}_{\text{B}}. \tag{2}$$

Here, J is the exchange integral, r is the distance between colliding radicals, $\mathbf{S}_{\text{A,B}}$ are the spin moment operators of the unpaired electrons of the radicals. The rate of flip-flop of two spins in the course of their bimolecular collisions in solution is given by the Smoluchowski equation

$$V = 4\pi r_{\text{ex}} DC, \tag{3}$$

Here, r_{ex} is the effective radius of the spin exchange for collisions Eq. (1), D is the coefficient of the mutual diffusion of two colliding radicals, C is the concentration of paramagnetic particles.

The best method for studying spin exchange in solutions is EPR spectroscopy, since with an increase in the rate of spin exchange Eq. (3), for example, from an increase of the concentration of spins (C), characteristic changes in the stationary EPR spectral shape occur. The rate of the spin exchange can also be varied by heating of a sample. An obvious consequence of the spin exchange between spins with different resonance frequencies of an inhomogeneously broadened EPR spectrum is a decrease in the lifetime of the spins with a certain resonant frequency. This leads to the exchange homogeneous broadening of the EPR lines of the spins.

Based on the above considerations, one would expect that with an increase in the rate of spin exchange, all resonance lines will become wider and wider. But everything turns out to be much more interesting. When a certain spin exchange rate is reached, the entire observed EPR spectrum visually converts to as a homogeneously broadened spectrum with a resonant frequency equal to the frequency of the center of gravity of the originally inhomogeneously broadened EPR spectrum! This effect is called the collapse of the inhomogeneously broadened spectrum into the homogeneously broadened spectrum. With a further increase in the spin exchange rate, the contribution of this spin exchange mechanism to the broadening of the resonance lines decreases. This behavior of the spectrum width with an increase in the spin exchange rate is called exchange narrowing of the spectrum.

Figure 1 illustrates the above-mentioned changes in the shape of the EPR spectrum for the simplest model system—a radical solution in which the EPR spectrum is split into two hyperfine structure components caused by the contact hyperfine interaction of an unpaired electron with a magnetic nucleus with spin $I = 1/2$ (calculation details are given in [11–13, 15, 16]).

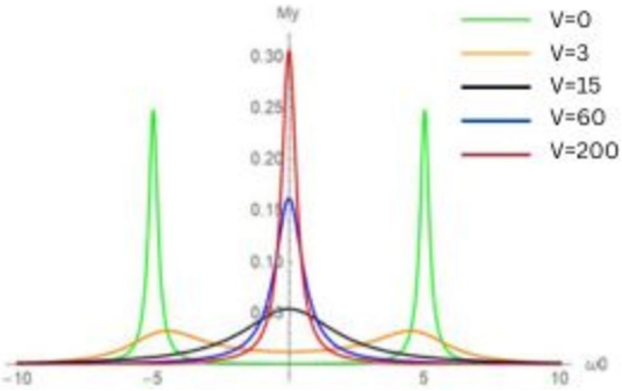

Fig. 1 Dependence of the shape of the EPR spectrum of a two-frequency model spin system on the spin exchange rate V. Calculations were performed for the following values of magnetic resonance parameters: $1/T_2 = 0.2$ Gs, $1/T_1 = 0.05$ Gs, $a = 10$ Gs. Spin exchange rate V and electron spin frequency ω_0 are also given in Gauss. Here are presented spectra for the Rabi frequency $\omega_1 = 0.01$ Gs (linear response case). To convert all these parameters into inverse seconds (units of angular frequency), they must be multiplied by the gyromagnetic ratio for electrons equal to $1.76\ 10^7$. These spectra are for the linear response regime at low microwave powers

It can be seen from Fig. 1 that with an increase in the exchange rate V, the two hyperfine components of the EPR spectrum first broaden and shift to the center of the spectrum, and then the entire spectrum merges (collapses) into one line. With a further increase in the rate of spin exchange, the contribution of spin exchange to broadening does not increase, but decreases. Asymptotically, with an increase in the spin exchange rate, the width of the entire spectrum tends to the width of the resonance line of an individual radical!

The resonant frequencies and widths of the EPR spectrum lines depend on the microwave field power [17].

Even at powerful saturating microwave fields, an increase in the rate of spin exchange causes similar transformations, but with some differences. The EPR spectrum collapses at a higher spin exchange rate compared to the linear response case [17].

2.2 A Widespread but Incorrect Interpretation of the Transformations of the EPR Spectrum Shape Presented in Fig. 1

Interpretation of these transformations of the EPR spectrum in dilute solutions of paramagnetic particles based on a *single-particle approach* is still widespread although based on an old paradigm of spin exchange. This approach served well for years, and it is important to appreciate that this is how exchange narrowing of EPR spectra has been usually interpreted.

In the limit of slow spin exchange, the broadening of resonance lines has been interpreted simply as a new (shorter) phase relaxation time T_2 for each spin, since bimolecular spin exchange acts as a parallel channel for phase relaxation of spins. The higher the rate of spin exchange, the greater the contribution of the spin

exchange to the broadening of the lines. And this qualitatively coincides with what is observed in EPR spectra at lower radical concentrations. But these arguments do not help to understand the effect of exchange narrowing on the spectrum in the case of fast spin exchange.

In the fast spin exchange limit case, the exchange narrowing of the spectrum under the old paradigm assumes that fast spin exchange averages to zero those spin interactions that cause inhomogeneous broadening of the EPR spectrum.

Spin exchange between radicals can be interpreted as the spectral diffusion, i.e., jumps of the electron spin resonance frequency between the frequencies of the hyperfine components of the EPR spectrum. In a course of this spectral diffusion, the frequency shift of the electron spins due to their interactions with magnetic nuclei will average to zero.

As a consequence, the hyperfine structure of the EPR spectrum should disappear, all electron spins will have the same resonant frequency. Heisenberg exchange interaction in radical collisions should not manifest itself in any way when radicals with the same resonant frequencies collide. In an ensemble of identical spins, the Heisenberg exchange interaction does not change the state of the spins.

This brief summary of the widespread description of the manifestation of spin exchange in EPR spectra contains interesting qualitative considerations that give the feeling that we seem to understand the problem well. But in fact, it is hard to be satisfied with this approach. These qualitative considerations give reasonable interpretation of the additional broadening of EPR lines by spin exchange only in the limit of slow spin exchange.

2.3 The New Paradigm of Spin Exchange Interprets the Shape Transformations of the EPR Spectrum in Terms of Collective Modes of Spin Motion, Strictly Speaking, Collective Modes of Motion of Partial Magnetizations of Spin Sub-ensembles with a Given Frequencies of EPR Transitions in Dilute Solutions

The common widespread reasoning missing the point that in a dilute solution, radicals spend most of the time in the time intervals between collisions. In the system under consideration, collisions are a slow process and the average time between collisions is a characteristic time of the experiment.

But a single collision of two radicals is a fast process. The duration of a single collision is much less than an average time of free movement of a radical between its two successive bimolecular collisions. The EPR signal observed in an experiment represents the response from spins between their collisions with each other. Therefore, it is not justified to first average the spin-Hamiltonian over a slow process, and then calculate the EPR spectrum in the time interval of a slow process. Note that to obtain the kinetic equations for the spin magnetizations, averaging over a fast process on a time scale of collisions of paramagnetic particles is used which is a reasonable procedure to find the effective (averaged) radius of spin exchange in Eq. (3) [4, 5, 13].

Today, we have an alternative approach to interpret the shape changes in the EPR spectrum: the new paradigm of spin exchange and its manifestations in the shape of EPR spectra [11–17]. It provides a consistent description of all these transformations of the EPR spectrum caused by the spin exchange for solutions of paramagnetic particles.

At low concentration of radicals, as a rule, the EPR spectra have a hyperfine structure (inhomogeneous broadening). Each hyperfine component of the spectrum corresponds to a certain configuration of the spins of the magnetic nuclei of the radical. To further analyze the motion of spins, we introduce sub-ensembles of radicals with a given configuration of nuclear spins, that is, sub-ensembles of radicals that give different hyperfine components of the EPR spectrum upon infinite dilution of the radical solution. Each of these radical sub-ensembles can be specified by the corresponding frequency ω_k and partial magnetization of the electron spins $M_k(\omega_k)$.

In the new paradigm of spin exchange, collective modes of motion of the partial magnetization of paramagnetic particles are formed in dilute solutions. Elementary excitations of these collective modes are quasiparticles and electron paramagnetic resonance (EPR) "pumps" these quasiparticles. The resonant frequencies of these quasiparticles (spin excitons) in the linear response regime are practically independent of the microwave power (see, e.g., [16]). Therefore, in linear response limit in the EPR spectrum, we detect the resonant frequencies of "free motion" of spins (without microwave field).

Beyond the linear response regime, the collective modes are combined states of spins and photons (spin polaritons) [18].

The resonance frequencies of the collective modes are the frequencies of the EPR spectral lines [16, 18]. The resonant frequencies and resonance widths for spin excitons and spin polaritons reveal very interesting properties which were analyzed comprehensively in [7–12, 16, 18].

Here, I will present only those properties of excited spin states that are of interest for the formation of a gas of quasiparticles (bosons) and their possible condensation.

As noted above, in the case of slow spin exchange, the main contribution to each collective mode of spin motion comes practically from only one spin sub-ensemble (see below Eq. (9)). By selectively exciting only one of the collective modes, it is possible to get a gas dominated by bosons that are selectively excited. But this gas of bosons does not have the maximum possible concentration, since not all spins of the system participate practically equally in its creation.

For fast spin exchange in the exchange narrowing regime, only one collective mode of motion is effectively excited. There are only identical bosons. In the limit of high spin exchange rate, we observe a single polariton resulting from the exchange narrowing effect. The resonant frequency of this polariton is the center of gravity of the EPR spectrum. This polariton should have a Lorentzian absorption lineshape. Under exchange narrowing, the observed EPR spectral line comes from excitation of all spins so that we can get a high concentration of identical bosons (polaritons).

It is well known that high microwave power broadens the resonance lines observed in the experiment. This broadening also occurs for the resonance line observed under exchange narrowing conditions. The question arises as to how much this resonance line broadening affects formation of the BEC.

With an increase in the microwave power (increase of photon density), the saturation effect appears. In addition, elementary excitations of a combined system of spins and photons (spin polaritons) appear. The resonant frequencies and linewidths of spin polaritons depend on the power of the microwave field [8, 11, 17].

It is expected that with an increase in the microwave power, the concentration of polaritons will increase. At first glance, it may seem that the broadening of the observed line due to the microwave field may interfere negatively with the formation of the BEC. Indeed, with an increase in the microwave field, the saturation effect manifests itself, and the width of the observed line increases as $1/T_{2\text{eff}}=(1/T_2)\ (1+\omega_1{}^2T_1T_2)^{1/2}$ [18], where T_1 and T_2 are the longitudinal and transverse relaxation times of the individual paramagnetic particles and ω_1 is the Rabi frequency of the microwave field.

Under saturation conditions, $\omega_1{}^2T_1T_2>1$, the line width $1/T_{2\text{eff}}$ could be much greater than $1/T_2$. We know that each polariton has a homogeneously broadened line. Therefore, following the uncertainty relation in quantum mechanics, we used to think that the broader resonance line means a shortening of the quantum coherence lifetime.

However, the broadening of the homogeneous line when saturation occurs has another cause. It does not mean that there is additional homogeneous broadening of the resonance line. It occurs because the center of a homogeneously broadened line is saturated more than its wings, in effect, broadening the observed spectral line by selectively decreasing intensity of the center. However, the lifetime of polaritons, or spin decoherence time, does not decrease with an increase in the power of the microwave field.

In this section of the manuscript, the main attention is paid to the effect of exchange narrowing of EPR spectra in dilute solutions of paramagnetic particles. According to the new paradigm of spin exchange, at relatively slow spin exchange, the microwave field excites a set of several different polaritons. But at a sufficiently high spin exchange rate, the microwave field excites only a single type of quasiparticles (identical polaritons, see Fig. 1), raising the prospect of obtaining a condensate of these polaritons.

Usually, the EPR spectrum has no structure and becomes rather uninformative at high spin exchange rates after an inhomogeneously broadened spectrum collapses. But with a further increase in the spin exchange rate, additional narrowing of the EPR spectrum occurs as the microwave field creates identical polaritons (bosons). Thus, the exchange narrowing of the EPR spectrum opens the way for creation and detection of a gas of identical bosons [11–17].

The exchange narrowing of the EPR spectrum in a dilute solution of free radicals is easily observed even at room temperatures. Thus, in principle, BEC is also feasible in dilute solutions of free radicals at room temperatures.

3 Prerequisites for Formation of BEC in Dilute Solutions of Free Radicals?

Prerequisite #1. There must be a mechanism to create identical elementary excitations, i.e., identical quasiparticles.

Where do quasiparticles with a coherent state of partial magnetizations of different sub-ensembles of electron spins come from? For ordered solids, it is usual to introduce collective modes, for example, magnons. The collective modes of motion of partial spin magnetizations in dilute solutions form, in effect, due to the recoil of the quantum coherence from the collision partner in each collision caused by the exchange interaction. This recoil of coherence is somewhat reminiscent of Newton's third law.

Paramagnetic particles diffuse in the liquid. From time to time, a pair of particles randomly collides. During the collision, the exchange interaction is briefly non-zero. As a result of the collision, the states of electron spins of both colliding particles change. And, at first glance, it is difficult to imagine that these random collisions can lead to any observable consistency, coherence, in the motion of the spins of different paramagnetic particle. In this regard, A. Abragam remarked in his book (see [18], pp. 277–278): "…one does not expect phase coherence to be introduced into a system through a coupling described by a random Hamiltonian". But it turns out it is possible!

Collective modes of motion are highlighted if we switch our focus from considering the motion of individual spins in the phase space to analyzing the averaged motion of sub-assemblies of spins with given resonant frequencies. This change of focus is achieved using the methods of kinetic theory.

The collective modes in dilute radical solutions are seen easily in the kinetic equations for the partial magnetizations of the different sub-ensembles of spins of the system [11–17]. Consider radicals in which an unpaired electron interacts with only one magnetic nucleus with spin $I=1/2$. In liquids, such a radical typically has two resonant frequencies $\omega_{01}=\omega_0+a/2$ and $\omega_{02}=\omega_0-a/2$. Here ω_0 is the Zeeman frequency of the unpaired electron in a magnetic field B_0, and a is the isotropic hyperfine interaction (HFI) constant of an unpaired electron with the magnetic nucleus. The ensemble of radicals is divided into two equal sub-ensembles, in one sub-ensemble the electron spins have the frequency ω_{01}, and in the other ω_{02}. We will consider the case that both sub-ensembles have the same relaxation time T_2 (according to Bloch [18]) and that the spin–spin dipole–dipole interaction to paramagnetic relaxation can be neglected. The contribution of the dipole–dipole interaction is discussed in [11–15, 19–21].

Formation of collective modes of spin motion induced by random bimolecular collisions is seen even in the simplest case where EPR is detected under *linear response* conditions. Then, the kinetic equations for the transverse partial magnetizations of the two sub-ensembles have the form [16, 21]

$$\begin{aligned}
\partial M_{1-}/\partial t &= (-i(\omega_0+a/2-\omega)-1/T_2)M_{1-}-(\mathbf{1/2})VM_{1-}+(\mathbf{1/2})VM_{2-}-i\omega_1 M_0/2;\\
\partial M_{2-}/\partial t &= (-i(\omega_0-a/2-\omega)-1/T2)M_{2-}-(\mathbf{1/2})VM_{2-}+(\mathbf{1/2})VM_{1-}-i\omega_1 M_0/2;
\end{aligned} \tag{4}$$

where $M_{k-}=M_{kx}-iM_{ky}$ and $\omega_1=\gamma B_1$ is the Rabi frequency of the electron spins in solution.

From the coefficients of the system of Eq. (4), we form the matrix L with $\mathbf{M}_0\equiv\{M_0/2, M_0/2\}$, giving

$$\partial \boldsymbol{M}_{-}/\partial t = \boldsymbol{L}\mathbf{M}_{-} - i\omega_1 \mathbf{M}_0; \tag{5}$$

$$\boldsymbol{L} = \{\{-i(\omega_0 + a/2 - \omega) - 1/T_2 - (1/2)V,\ (1/2)V\},$$
$$\{(1/2)V,\ -i(\omega_0 - a/2 - \omega) - 1/T_2 - (1/2)V\}\}.$$

We find the eigenvalues $\{\lambda_k\}$ of the operator $\boldsymbol{L}$ from the equation

$$|\boldsymbol{L} - \lambda \boldsymbol{E}| = 0, \tag{6}$$

where $\boldsymbol{E}$ is the unit operator. Each eigenvalue corresponds to an eigenvector $\mathbf{X}_k$, which satisfies the equation

$$L\mathbf{X}_k = \lambda_k \mathbf{X}_k. \tag{7}$$

$$\mathbf{X}_{\mathrm{k}} = u_{k1} M_{1-} + u_{k2} M_{2-},\ k = 1,\ 2.$$

For the two-frequency model system,

$$\lambda_1 = -i(\omega_0 - \omega) - R/2 - 1/T_2 - V/2; \lambda_2 = -i(\omega_0 - \omega) + R/2 - 1/T_2 - V/2;$$

$$X_1 = c_1\{-((ia + R)/V)M_{1-} + M_{2-}\}; X_2 = c_2\{-((ia - R)/V)M_{1-} + M_{2-}\}; \tag{8}$$

where $R = (-a^2 + V^2)^{1/2}$ and c_1, c_2 are normalization coefficients.

The resonant frequencies ω of the collective modes are found from the condition $\mathrm{Im}\{\lambda_k\} = 0$ and the widths of the corresponding EPR lines are $\mathrm{Re}\{\lambda_k\}$ [11, 12, 15–17].

For relatively slow spin exchange ($V < \mathrm{mod}(a)$), the unnormalized collective modes Eq. (8) are

$$X_1 \approx -iM_{1-} + (V/(2a))M_{2-}; X_2 \approx i(V/(2a))M_{1-} + M_{2-}; \tag{9}$$

For relatively slow exchange with $V/\mathrm{mod}(a) < 1$, collective modes are roughly the motion of one partial magnetization with a small contribution from the other partial magnetization.

For fast spin exchange $V >> \mathrm{mod}(a)$ and the collective modes Eq. (8) asymptotically approach

$$\mathbf{X}_1 = \left(1/2^{1/2}\right)\{-M_{1-} + M_{2-}\}; \mathbf{X}_2 = \left(1/2^{1/2}\right)\{M_{1-} + M_{2-}\}; \tag{10}$$

In this limit, both partial magnetizations make equal contributions to the collective modes. But at the same time, the collective modes Eq. (10) fundamentally differ concerning the phases of the partial transverse magnetization of the spin sub-ensembles. For this two-frequency model system, under conditions of exchange narrowing, the partial magnetizations of the two sub-ensembles precess with the same phase ($\mathbf{X}_2$) or the phases differ by 180° ($\mathbf{X}_1$), since $\exp(\mathrm{i}\pi) = -1$ (see Eq. (10)).

The eigenvectors $\mathbf{X}_k$ represent a coordinated or coherent movement of the transverse partial magnetizations of the sub-ensembles of radicals. Despite

random collisions of radicals, a definite relationship between the transverse partial magnetizations and their precession phases, characteristic of only a given eigenvector $\mathbf{X}_k$, is maintained.

The important point is that under conditions of exchange narrowing, the microwave field pumps quasiparticles of practically only the collective mode $\mathbf{X}_2$ (see Eq. (10)).

The eigenvectors of $\boldsymbol{L}$ are superpositions of the partial transverse magnetizations $\mathbf{M}_{k-}$ of spins belonging to different sub-ensembles of spins. In fact, these eigenvectors are the independent collective modes (degrees of freedom) of the quantum coherence of the system (see Eq. (7)). Each collective mode gives its own resonant response to an external microwave field at ω.

The resonant frequencies of the collective modes and their widths can be found by minimizing mod(λ_k) with respect to the microwave frequency [11–17]. To minimize λ_k, its imaginary part should become zero.

For example, for the two-frequency model system in the linear response regime, the values of the resonant frequencies Ω_s and their widths $\Delta\omega_k$ are (see Eq. (8), [16])

$$\Omega_1 = \omega_0 - (1/2)\mathrm{Im}\{(-a^2 + V^2)^{1/2}\}; \Omega_2 = \omega_0 + (1/2)\mathrm{Im}\{(-a^2 + V^2)^{1/2}\}; \quad (11)$$

and

$$\begin{aligned} \Delta\omega_1 &= 1/T_2 + V/2 + (1/2)\mathrm{Re}\{(-a^2 + V^2)^{1/2}\}; \\ \Delta\omega_2 &= 1/T_2 + V/2 - (1/2)\mathrm{Re}\{(-a^2 + V^2)^{1/2}\}. \end{aligned} \quad (12)$$

Several observations can be made from these equations:

In the region of slow spin exchange $V < \mathrm{mod}(a)$, the resonance width of both collective modes is the same and is equal to $\Delta\omega_1 = \Delta\omega_2 = 1/T_2 + V/2$, since Re$\{R\}$ is zero;

The collapse of the spectrum occurs when the condition $V = \mathrm{mod}(a)$ is fulfilled, since at $V > \mathrm{mod}(a)$, the resonant frequencies of both modes of collective motion coincide with the average frequency of the spectrum: $\Omega_1 = \Omega_2 = \omega_0$;

In the region of the exchange narrowing of the spectrum, the resonance widths of the collective modes are different. From second order perturbation theory with respect to the small parameter $\mathrm{mod}(a)/V << 1$, the resonance widths of the collective modes are

$$\Delta\omega_1 = 1/T_2 + V - a^2/(4V) \text{ and } \Delta\omega_2 = 1/T_2 + a^2/(4V). \quad (13)$$

One of the modes gives a resonance, whose width continues to increase in the region of fast spin exchange, and the second mode gives a resonance whose width decreases with increasing spin exchange rate, for example, with increasing concentration of radicals. Asymptotically, the resonance width of the second mode approaches the intrinsic width of the isolated radical with increasing spin exchange rate: exchange narrowing of the EPR spectrum. The spin exchange contribution to the width $\Delta\omega_2$ (see Eq. (13)) decreases with increasing rate of spin exchange as $a^2/(4V)$.

In the conditions of exchange narrowing, not only the widths of the EPR lines of the two collective modes $\mathbf{X}_1$ and $\mathbf{X}_2$ Eq. (10) behave completely differently [16]. They have completely different integral intensities! The *integral intensity* of the wide line ($\mathbf{X}_1$) tends to zero with an increase in the spin exchange rate. And the integral intensity of the exchange narrowed line $\mathbf{X}_2$, on the contrary, increases with an increase in the rate of spin exchange. As a result, we get that at a high rate of spin exchange, only one collective mode is practically excited. This creates good prerequisites for BEC.

Here, I presented some analytical results concerning collective modes Eqs. (7–13) just to illustrate how I treat the problem. With this goal, I presented protocol of calculations for the simplest model situation of low microwave power (linear response case). In fact, collective modes are created at any microwave power. Spins and microwave photons create combined states-polaritons.

For two-frequency model, the analytical solutions were obtained in some cases also in presence of high microwave power [11, 17].

At an arbitrary microwave power, even for a two-frequency model, it is necessary to solve a cubic equation to find the eigenvalues and eigenvectors of the equations (like Eqs. (6, 7)) [11, 17]. Solutions are given by cumbersome algebraic expressions. Therefore, I am not quoting these cumbersome expressions, they are already in published articles. They are analyzed numerically in detail in works [7, 8, 11, 17]. All calculations show that collective modes of coherent motion of magnetizations of sub-ensembles of spins are formed not only at zero power of the microwave field as it is shown on Eqs. (5–10), but at any microwave power.

Elementary excitations of those collective modes of combined motion of magnetizations of sub-ensembles of spins and microwave photons I call polaritons.

A detailed analysis of these resonant frequencies, the broadening of resonances and, in general, the shape of the EPR spectrum depending on the spin exchange rate in presence of the microwave field of arbitrary power is in [11–17].

Prerequisite #2. Quasiparticles must be bosons so that many identical quasiparticles can be in the same state.

Let us explore why elementary excitations of spins in dilute solutions of free radicals are bosons at arbitrary power of microwave field in order to satisfy another BEC prerequisite.

Elementary excitations of collective modes of motion are quasiparticles that obey Bose–Einstein statistics. This follows from the fact that at any power of the microwave field, the kinetic equations for partial magnetizations of the spin sub-ensembles with given resonant frequencies of electron spins are described by a system of linear equations with constant coefficients [12–14]

$$\partial \mathbf{X}_k(t)/\partial t = L\mathbf{X}_k(t) + L_e\mathbf{X}_k(0) \tag{14}$$

The eigenvectors of the operator $\boldsymbol{L}$ (Eqs. (7–8)) have remarkable properties. They form a complete orthogonal basis of the collective modes of motion, that is, any motion of partial magnetizations can be represented as a unique linear superposition of these eigenvectors. Without additional perturbation, each eigenvector moves

independently of the others. The microwave field can excite different eigenvectors of the motion operator $\boldsymbol{L}$.

Excitation of a given eigenvector creates a quasiparticle (spin excitons without microwave field or spin polaritons in presence of microwave field).

Differentiating Eq. (14), we obtain

$$\partial^2 \mathbf{X}_k / \partial t^2 = \lambda_k^2 \mathbf{X}_k, \tag{15}$$

The motion of the quasiparticles in question is described by the equation of a damped harmonic oscillator. Consequently, these quasiparticles obey Bose–Einstein statistics, and there can be many identical quasiparticles in the system at the same time. And these bosons, in principle, can form a BEC.

Prerequisite #3. The quasiparticles must be sufficiently long-lived.

Exchange narrowing of the EPR spectrum creates a gas of identical long-lived quasiparticles which is one the basic prerequisites for BEC formation.

It arises due to the fast coherence transfer between paramagnetic particles during their random bimolecular collisions.

At any rate of spin exchange, the observed EPR spectrum is the sum of contributions from the resonant responses of all collective modes to an external alternating field. The frequencies and widths of the resonant lines are given by the eigenvalues of the operator L (e.g., see Eqs. (5–8) for a simple model situation). Calculations for model systems show that even under exchange narrowing, different collective modes have different resonant frequencies (except for the two-frequency system [16]). For radicals with a single magnetic nucleus with spin $I=1$, for example, ^{14}N, the EPR spectrum has three hyperfine components with resonant frequencies ω_0+a, ω_0, ω_0-a, at low spin exchange rate ($V\to 0$). Under conditions of exchange narrowing of the EPR spectrum, the resonant frequencies of the collective modes, which give the outer-lines with resonant frequencies (ω_0+a) and (ω_0-a) at $V\to 0$, shift to the center of the spectrum, ω_0, but the asymptotic shift at $V\to\infty$ does not give equal frequencies (ω_0, ω_0, ω_0) for those three lines. The asymptotic resonance frequencies in the case of free motion are ($\omega_0+a/\sqrt{3}$, ω_0, $\omega_0-a/\sqrt{3}$) (see [16], Eq. (5.41)].

For slow spin exchange, we have a mixture of different quasiparticles (bosons) with short lifetimes. However, fast spin exchange offers better conditions for boson condensation. Indeed, after the onset of spectral narrowing, the random exchange interaction during a collision has a negligible effect on spin decoherence and on the excitation lifetime of the observed collective mode $\Delta\omega_2=1/T_2+a^2/(4V)\approx 1/T_2$, Eq. (13). Consequently, with fast spin exchange, $V>>a$, the microwave field excites the collective mode with the spin decoherence time that nearly coincides with the decoherence time of isolated spins T_2. For nitroxide radicals, this time is on the order of microseconds at room temperatures [6].

Therefore, it can be argued that the exchange narrowing case provides the prerequisites for formation of a BEC of quasiparticles in dilute solutions of paramagnetic particles.

For comparison, we note that in the slow spin exchange limit, all quasiparticles manifest themselves in the EPR spectrum, but spin exchange can reduce their spin

phase relaxation time by orders of magnitude [4–6]. Therefore, bosons gas created in the limit of slow spin exchange are not suitable for BEC formation.

Thus, the exchange narrowing observed in the experiment does not mean that all collective modes have the same resonant frequency. Each collective mode gives a resonant line; but the intensity of each line is determined by how the microwave magnetic field excites that collective mode. In fact, the observed exchange narrowing of the spectrum into one narrow homogeneously broadened line is due to the fact that the external alternating B_1 field effectively excites only one of the collective modes of the ensemble [12–14].

The collective mode with the narrowest resonance line is the line observed in the exchange narrowed EPR spectrum!

The remaining collective modes in the situation of exchange narrowing have a small matrix element for excitation by the microwave field, their resonances are broad, and they give resonant lines with low amplitudes and low integral intensities. They can be considered "forbidden" lines that are weakly expressed on the wings of the intense exchange-narrowed line. That line is associated with the excitation of a specific mode of collective motion of sub-ensembles with different resonant frequencies.

Prerequisite #4. There must be a sufficiently high concentration of quasiparticles (spin polaritons) so that the gas of identical spin polaritons can turn into a BEC.

The density of identical bosons can be controlled by the concentration of radicals and the power of the microwave field (density of photons).

The density of quasiparticles increases proportionally to the concentration of paramagnetic particles.

The density of spin polaritons might reach a plateau or pass a maximum when the microwave power increases and saturates the spin system. At room temperature, the maximal spin polariton density might be estimated from the radical concentration C as $N \approx (\hbar\omega_0/kT)\ C$, where k is the Boltzmann constant, and T is temperature. In typical X-band EPR spectrometers $N \approx 10^{-3}\ C$. With $C \sim 100$ mM/L then the spin polariton density might be $\sim 10^{19}$ cm^{-3}.

As already noted, it is important that the lifetime of the excited state of the collective mode be long since the longer the lifetime of the excited quasiparticles, the greater the stationary concentration of quasiparticles.

4 Where to From Here? Next Experiment Required

There are still many questions about the Bose–Einstein condensation of spin polariton gas, which is created under conditions of exchange narrowing of EPR spectra. With the hope of obtaining additional information about the condensation of bosons in the situation under consideration, the following experiment can be proposed.

Under conditions of exchange narrowing of the EPR spectrum, we expect that the magnetization $\mathbf{M}$ of the system is described by one specific spin polariton $\mathbf{X}_k(\omega_1)$ (see Eq. (15)). Each polariton performs nutations at its characteristic frequency and with a characteristic paramagnetic relaxation time that depends on the power of the microwave field. Let's suddenly turn off the microwave field and observe the

free induction signal (FID). Remembering that immediately before switching off the microwave field, the magnetization of the spins was a specific eigenvector of the magnetization $\mathbf{X}_k(\omega_1)$, one may mistakenly think that the FID signal will exponentially decrease with the characteristic spin decoherence time for that particular polariton while oscillating with the characteristic frequency of that polariton.

In fact, after switching off the microwave field, the system has a different orthogonal and full set of eigenvectors $\mathbf{X}_{0k}$ at $\omega_1 = 0$ appropriate for the free motion of the spins. In this case, the magnetization of the spins at the moment of switching off the microwave field, $\mathbf{X}_k(\omega_1)$, must be represented in the basis of the eigenvectors for the free movement of the spins with no microwave field. Thus, the FID is the sum of decaying oscillations for the new eigenvalues. In any case, the decay of the FID will not be described by a single exponent. By changing the power of the pumping field, we change the ratio of contributions to the FID from different collective modes of free movement.

Analysis of such experimental data can confirm the formation of a Bose–Einstein condensate. So far, we can confidently assert that we can obtain a gas of identical bosons at room temperature.

5 Summary

This work proposes a new approach to realize the Bose–Einstein condensate in dilute solutions of paramagnetic particles at room temperature. This approach is based on the new paradigm of spin exchange in EPR spectroscopy, which uncovered that spin exchange creates collective modes of motion from sub-ensembles of spins with discrete sets of resonance frequencies [12–17] and found experimental confirmations (see, e.g. [7–10]).

In summary, in this article, I demonstrate that using EPR methodology we can satisfy BEC pre-requisites for dilute solutions of paramagnetic particles at room temperature formulated. Below is a brief summary of how these prerequisites are satisfied.

#1. The random bimolecular collisions of particles form collective modes of motion for the partial magnetizations of sub-ensembles of paramagnetic particles with different resonance frequency. Elementary excitation of those collective modes creates corresponding quasiparticles. Each collective mode is a coherent precession of partial magnetizations of different sub-ensembles of spins on a macroscopic scale [10–15, 21].

Collective modes are formed due to the recoil effect in the process of bimolecular spin collisions. At thermodynamic equilibrium with $B_1 = 0$, macroscopic quantum coherence does not occur, since at $B_1 = 0$ the transverse components of the magnetization vectors have random values and random orientations.

The above results allow us to formulate a protocol for obtaining the boson gas. One can take a dilute solution of radicals and examine the shape of the CWEPR spectrum. Increasing the rate of spin exchange by increasing the concentration of radicals and/or temperature can narrow the CWEPR spectrum so much that the one observed line has the width of an individual resonant line of an isolated radical.

#2. Following the mechanism described above, we obtain a constant number of identical excitations or quasiparticles in solution, that is, a gas of identical bosons. The concentration of bosons depends on the concentration of paramagnetic particles, on the power of the microwave field, and on the lifetime of the bosons.

#3. At a slow spin exchange rate, the microwave field produces a whole set of collective modes and we obtain a mixture of several short-lived boson gasses.

Under the conditions of exchange narrowing, the microwave field produces the longest-lived bosons in only one particular collective mode. Thus, there is a possibility to create a boson gas of high enough density.

Under the condition of the fast spin exchange, the microwave field excites only one collective mode, namely, the most long-lived collective mode.

#4. The maximum number of elementary spin excitations at room temperature, N, can be estimated as $N \approx (\hbar\omega_0/kT)\ C$.

Therefore, there might be enough bosons to give a condensate.

Under the conditions when the EPR spectrum manifests exchange narrowing, the necessary pre-requisites for BEC formation are satisfied.

Although the BEC prerequisites are satisfied, it remains to be shown whether the gas of bosons does condense to form BEC or if it is a new peculiar dynamic regime of collective, synchronized, and coherent motion of partial magnetizations in dilute solutions of paramagnetic particles. This is an area for future research.

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Declarations

Conflict of Interest The author declares no competing financial interest.

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