EPR and development of quantum electronics

A A Manenkov
Prokhorov General Physics Institute RAS, Moscow, Russia
E-mail: manenkov@kapella.gpi.ru

Abstract. A role of electron paramagnetic resonance in development of quantum electronics is discussed. Basic principles and history of masers are briefly described. Spin-levels of paramagnetic ions in crystals as a very suitable object for active media of solid-state masers (called as EPR-masers) and physical processes in EPR-masers (population inversion of energy states) are analyzed. This analysis demonstrates a significant role of relaxation processes in multi-level spin-systems for efficient maser action. In this context peculiarities of spin-lattice and spin-spin cross relaxation processes in multi-level systems are analyzed. Development of EPR-masers and their application in radioastronomy and far-space communication systems are briefly described.

1. Introduction
Studies of electron paramagnetic resonance phenomenon (EPR) discovered by E. K. Zavoiskiy in 1944 made a very strong impact on a development of modern physics and other sciences (chemistry, biology, etc), and very wide applications. These studies significantly affected also the development of quantum electronics. By now a great number of review papers and books was published in which different aspects of EPR physics and various applications including in quantum electronics were described (see, for instance [1, 3, 4]). In one’s turn the development of quantum electronic (QE) had a positive feedback – it significantly influenced further development of researches in EPR field.

In this paper the author aims to analyze briefly both aspects of EPR-QE connection. The plan of the paper includes:

· description of basic principles of QE and a brief history of masers,
· analysis of spin levels of paramagnetic ions in crystals as an object of active media of solid-state masers (we will call this type of masers as EPR-masers)
· analysis of physical processes in EPR-masers: inversion of spin level populations
· a brief description of EPR-masers development and application
· analysis of relaxation processes in multi-level spin-systems.

2. Basic principles and brief history of quantum electronics
Quantum electronics as a new field of physics has originated in a middle of 50-th of XX century from the research works in microwave spectroscopy of gases. Two research groups, Basov and Prokhorov in the USSR and Townes and coworkers in the USA, have led independently to an idea of using

1 The history of the discovery is described in details by Zavoiskiy collaborators S. A. Altshuler and B. M. Kozyrev[1], and his daughter N. E. Zavoiskaya [2]
stimulated emission of radiation of molecules in molecular beams to generate an electromagnetic radiation [5,6].

The first molecular oscillator (called later a maser), based on this principle, has been realized on the ammonia molecular beam [6]. An inversion of energy level populations relative to a thermodynamically equilibrium state, required for exceeding stimulated emission over stimulated absorption, was obtained by passing the molecular beam through an inhomogeneous electric field. A positive feedback in the oscillator was realized in a microwave resonator through which molecules in an upper energy state were passed.

In 1955 a new method for population inversion in molecular beams was proposed by Basov and Prokhorov [7] – the method based on excitation of molecules by auxiliary radiation (pumping). An essence of the method is explained in figure 1 for a 3-level molecule system in which auxiliary radiation with frequency $\nu_{\text{aux}}$ induces a resonance transition between low and upper levels and at high enough power produces the inversion of a populations of one of these levels and an intermediate level. Thus, the oscillation conditions at $1 \rightarrow 2$ transition frequency $\nu_{\text{osc}}$ are produced.

![Figure 1. Schematic illustration of population inversion in two configurations of energy levels using auxiliary radiation at frequency $\nu_{\text{aux}}$; $\nu_{\text{osc}}$ is signal frequency at which oscillation can be obtained. After Ref. [7].](image)

Though this method has been proposed by Basov and Prokhorov for molecular beams, it is, obviously, universal one -applicable to any multi-level atomic systems. Basing on this idea the author of these words analyzed a possibility of population inversion in the ground-state spin-level system of Cr$^{3+}$ ions in ruby which by that time (1955) have been well studied: energy levels and corresponding wave functions have been determined [8,9]. An analysis showed that the spin-level system of Cr$^{3+}$ in ruby is very suitable for realization of e-m pumping method. The results of this analysis became a basis for our subsequent works on EPR-masers (see below for more details).

In 1956 Bloembergen analyzed the conditions for population inversion in a three-level spin-system by e-m pump in continuous-wave regime [10]. His analysis has shown that e-m pump can be very effective method for creation of solid-state masers.²

Later on the author of these words has generalized Bloembergen analysis considering besides stationary condition for inversion also a transient process of inversion during a pump pulse [14]. Since such a consideration is of interest for more complete understanding of pumping process in both stationary and non-stationary regimes we will present below its results in some details.

The three-level system with energies $E_3 > E_2 > E_1$ was considered [14] in which pump radiation at frequency $\nu_{\text{pump}} = (E_3 - E_1)/h$ induced transitions between levels $E_1$ and $E_3$ producing, at definite conditions, the population inversion for $3 \rightarrow 2$ or $2 \rightarrow 1$ transitions. A change in time of level populations $n_i$ ($i=1,2,3$) under the pump radiation and spin-phonon interaction is described by the following rate equations:

² Note that N.Bloembergen came to the idea of population inversion by auxiliary radiation proceeding from other considerations: he refers in [10] to Pound’s and Overhauser’s works [11,12] on nuclear magnetic resonance and nuclear polarization (see also Bloembergen’s paper [13] in which he discusses especially his approach).
\begin{align}
\dot{n}_1 &= -(w_{13} + w_{12} + W_{13})n_1 + w_{21}n_2 + (w_{31} + W_{31})n_3 \\
\dot{n}_2 &= -(w_{21} + w_{23})n_2 + w_{12}n_1 + w_{32}n_3 \\
\dot{n}_3 &= -(w_{31} + w_{32} + W_{31})n_3 + (w_{13} + W_{13})n_1 + w_{23}n_2 
\end{align}

(1)

where $W_{13}$, $W_{31}$ and $w_k$ are transition probabilities induced by pump radiation and spin-phonon interactions, respectively. According to a quantum theory of thermodynamic equilibrium in atomic systems, the probabilities of radiation-induced and phonon-induced transitions obey the conditions:

$W_{13} = W_{31} = W$ and $w_k = w_k \exp \left( -\frac{E_k - E_i}{kT} \right)$.

**Figure 2.** Temporal evolution of inversion coefficient in active medium during pumping, switched on at $t = 0$, at various values of relaxation parameter $\alpha = \alpha_0 (\omega_{23} + \omega_{21})^{-1}$. The parameter $\tau = (2/3)(\omega_{23} + \omega_{21})^{-1}$ is relaxation time. After Ref. [14].

From a solution of rate equations the following expression for the inversion coefficient $J_{21}(t) = \chi(t)/\chi_0$ (where $\chi(t) = n_2 - n_1$ is a current population difference of levels 2 and 1 and $\chi_0 = (n_2 - n_1)_0$ is an initial population difference of these levels at $t = 0$, when the pump pulse is just switched on) has been obtained:

$$J_{21}(t) = -\frac{V_{13}}{2V_{21}} \exp \left[ -\left( 2W + \frac{3}{2} \frac{\omega_{23} + \omega_{21}}{\omega_{23} + \omega_{21}} \right) t \right] + \frac{V_{31}}{2V_{21}} (1 - 2\alpha) \exp \left[ -\frac{3}{2} \frac{\omega_{23} + \omega_{21}}{\omega_{23} + \omega_{21}} t \right] + (J_{21}),$$

(2)

where $\alpha = \frac{\omega_{21}}{\omega_{23} + \omega_{21}}$, $(J_{21})$, is the stationary inversion coefficient.
The inversion coefficient is the important parameter characterizing amplification properties of an active medium: at \( J_2 > 0 \) it amplifies an incident radiation, whereas at \( J_2 < 0 \) it absorbs the radiation. A value and temporal dependence of the inversion coefficient significantly vary with the relaxation parameter \( \alpha \). Figure 2 demonstrates these variations of \( J_2 (t) \) computed from (2).

The presented analysis shows that relaxation processes in active media are very important for determining conditions for most efficient maser action. Above theoretical results have been confirmed in experimental studies of amplification characteristics of ruby and \( \text{Cr}^{3+}:\text{TiO}_2 \) masers [14]. For example, figure 3 shows an output signal shape observed in the \( \text{Cr}^{3+}:\text{TiO}_2 \) maser (\( \lambda_{\text{signal}} = 10 \text{ cm} \)) at pulsed pumping.

![Figure 3. Oscillogram of the output signal observed in \( \text{Cr}^{3+}:\text{TiO}_2 \) maser amplifier at pulsed pumping. A sharp increase of the signal is seen at the beginning of pump followed by its transient decrease to the end of pump and relaxation decay after its switching off. Duration of the pump pulse is 8 msec.](image)

After Ref. [14].

### 3. Development and application of EPR-masers

Several research groups in USA and USSR have realized the first EPR-masers in 1957-1958. As active media they used different paramagnetic ions in crystals: \( \text{Gd}^{3+} \) in ethylsulfate [15], \( \text{Cr}^{3+} \) in cyanide[16, 17], and \( \text{Cr}^{3+} \) in corundum (ruby) [18-20].

Later on the other crystals as maser materials have been studied: \( \text{Cr}^{3+} \) and \( \text{Fe}^{3+} \) in \( \text{TiO}_2 \) and tungstates, \( \text{Gd}^{3+} \) in \( \text{CaF}_2 \) and others (see [4] for a review). The studies have shown that ruby is the most effective maser material possessing a unique combination of properties: a large crystalline field splitting of the ground-state (Kramers doublets), low dielectric losses, a long spin-lattice relaxation time, a high thermal conductivity, high chemical and mechanical stability. Using this material, masers in a wide spectral range, from dm to mm wavelengths, have been created. One of the first laboratory ruby masers created at Lebedev Physical Institute is shown in figure 4.

Masers as amplifiers of electromagnetic radiation possess an ultimately low intrinsic noise (which is due to spontaneous emission in an active medium) [4]. This important property makes them very attractive for application as high-sensitivity receivers in the microwave spectral range. In 1960-1970\(^{th}\) at some academic and industrial laboratories of the USSR ruby masers have been worked out and applied in radioastronomy and space communication systems [21]. Owing to their use a number of new important results in space research has been obtained. In particular, detail studies of space hydrogen radiation at 21 cm wavelength and discovery of new radiation lines of highly-excited hydrogen atoms at 8 mm spectral range (Sorochenko et al. [22]) gave valuable data on a distribution and characteristics (temperature, density, dynamics) of hydrogen in Galaxy.
Studies of maser emission from space at 1.35 cm (Matvienko et al. [23-25]) discovered earlier by Townes and coworkers [26], have presented very interesting data on a water content in some space sources. The use of EPR-maser amplifiers in planet radar systems allowed to obtain new data on characteristics of Mercury, Venus, Mars, Jupiter (Kotelnikov et al. [27]).

**Figure 4.** Ruby maser created at Lebedev Physical Institute in 1958: a -general view; b, c – fragments; b - signal and pump waveguides, pump source (klystron), c –two-frequency resonator. Signal and pump wavelengths are 15 cm and 2.21 cm respectively. After [19].

### 4. From masers to lasers

A successful development of microwave EPR-masers stimulated an extension of quantum electronics principles to shorter wavelength region. The fact that the first optical maser (laser) has been realized [28] on ruby as the active material was not accidental. Indeed, to that time (1960) physics of microwave ruby masers was well developed and optical spectra of this crystal were studied in details.

Creation of the first laser led to a rapid development of quantum electronics. Intensive studies were started of lasers using different type materials as active media: crystals and glasses activated with ions of transient group elements, atomic and molecular gases, semiconductors, etc.

Investigations in EPR and EPR-maser fields determined many directions in solid-state laser studies. In particular, EPR spectroscopy became an important tool for studies of crystals doped with Fe and RE group ions as active laser materials. Similarity of many processes in masers and lasers was very useful in studies of laser dynamics.

In one’s turn, investigations in maser-laser field stimulated further development in EPR physics. In particular, studies of physical processes in EPR-masers and solid-state lasers (population inversion, transient processes, saturation effects, etc) stimulated a development of studies of relaxation processes in crystals. Some results obtained in these studies are briefly described in the next section. They relate to features of relaxation processes in multi-level spin-systems.

### 5. Relaxation processes in multi-level systems

Make several general comments on a nature and a role of relaxation processes in multi-level spin-systems.

Two types of interactions determine a thermodynamic equilibrium in such the systems: spin-lattice and spin-spin cross relaxation. The first type interaction depends naturally on a crystal lattice temperature, and a character of this dependence is determined significantly by a mechanism of a spin-photon interaction. For elucidating the fundamental mechanisms of such interaction, a temperature dependence of a spin-lattice relaxation time in paramagnetic crystals was a subject of many theoretical and experimental studies still in pre-maser period, and especially in the maser-time in a connection with practical problems of quantum electronics. It relates, specifically, to the low (liquid helium) temperature range where, as a rule, EPR-masers work.
As far as the second type interactions, spin-spin cross-relaxation, interest to their studies appeared in connection with quantum electronics. Bloembergen and co-authors were the first who paid an attention to a role of cross-relaxation in spin-systems. They presented a theory of resonance cross-relaxation [29]. This work stimulated studies of cross-relaxation phenomena in more complex multi-level systems. Both types of interaction, spin-lattice and spin-spin cross-relaxation, play the fundamental role in physics of EPR-masers determining a possibility of population inversion in spin-energy levels, transient processes and saturation effects in maser amplifiers and oscillators. Cross-relaxation processes are characteristic ones also for multi-level systems used in solid-state lasers. A comprehensive analysis of the role of relaxation processes in masers was presented in many review papers and books (see, for example, [3, 4]).

After these general comments we will present below two results obtained in studies of spin-lattice and spin-spin cross-relaxation in multi-level systems.

1. In studies of spin-lattice relaxation the peculiarities of temperature dependence of relaxation times in liquid helium temperature range have been revealed: strong (exponential) dependence for lower doublets [30, 31] and, in contrast, very weak dependence for upper doublets [31]. The first of these results, the exponential temperature dependence of relaxation times, have been interpreted on the basis of two different models: as a resonance two-phonon Raman process [32, 33] (called in some papers as Orbach process) and as a specific case of one-phonon resonance process in multi-level systems [34]. A comprehensive analysis of these models based on quantum field theory has shown [35] that the latter is the most adequate model. Essence of this model is illustrated in figure 5 on an example of relaxation in a three-level system.

Relaxation transition probabilities $w_{ik}$ between corresponding levels (i, k = 1,2,3) in this system are supposed to be due to the one-phonon resonance processes. An analysis has shown [34] that relaxation kinetics of populations of energy levels in this system has, in general, a complex (non-exponential) character depending on all transition probabilities involved. However, in some specific cases of ratio between probabilities it can be one-exponential.

![Figure 5. Relaxation transitions in tree-level system (wavy lines with corresponding transition probabilities $w_{ik}$)](image)

For example, at $w_{12}, w_{21}<<w_{23}, w_{32}, w_{13}, w_{31}$ the levels 1 and 2 relax via the upper level 3. In the other case, if $w_{23}, w_{32}<<w_{12}, w_{21}, w_{13}, w_{31}$ the levels 2 and 3 relax via the lower level 1. Temperature dependence of relaxation rates predicted for these two cases, respectively for lower and upper doublets, are as follows:
\[ T_i^{-1} \propto \exp(\Delta/kT) - 1 \]  
\[ T_i^{-1} \propto [1 - \exp(-\Delta/kT)]^{-1} \]

where \( \Delta \) is an energy gap between levels 1 and 3.

Experimental data on the temperature dependencies of relaxation times observed in some crystals doped with ions of iron group and rare earth ions [30, 31, 36] are in a good agreement with these predictions confirming the adequacy of the model suggested in [34].

2. In studies of relaxation processes in crystals, containing multi-level paramagnetic ions, strongly pronounced cross-relaxation effects were observed. Thus, in ruby (four-level system) besides resonance (two-spin) energy exchange between spin levels more complex multi-spin processes - harmonic and combinative - have been revealed [37]. Figure 6 illustrates such the processes.

If the energy difference between a, b and a’, b’ levels satisfy the condition '':

\[ \Delta E_{ab} \approx \Delta E_{a'b'} \]

or

\[ m\Delta E_{ab} \approx n\Delta E_{a'b'} + l\Delta E_{cd} \]

where \( m,n,l \) are numbers of spins participating in the processes, harmonic or combinative cross-relaxation takes place.

Theoretical analysis based on a kinetic model of cross-relaxation showed a good agreement with experimentally observed features [37] demonstrating a high efficiency of such processes in multi-level systems. Cross-relaxation processes revealed at rather high concentrations of paramagnetic ions, influence significantly on inversion of populations of energy levels in maser active media, and, hence, on the efficiency of the maser.

![Figure 6](image-url)

**Figure 6.** Schematic illustration of cross-relaxation processes revealed in ruby [37]: (from right to left) resonance (two-spin), harmonic (four-spin), and combinative (five-spin).

A significance of cross-relaxation processes refers in equal degree to both microwave and optical masers using ion-doped crystals as active materials. In this context note that multi-particle cross-relaxation processes similar to those revealed in spin-systems [37] were observed also in optical levels of rare earth ions in crystals [38, 39].

6. Conclusions

Summarizing the brief analysis presented in this paper of the role of electron paramagnetic resonance in development of quantum electronics emphasizes several the most important, to our view, points.

The idea to use multi-level spin systems of paramagnetic ions in crystals as the active media of quantum amplifiers turned out very fruitful. It has led to creation of microwave quantum amplifiers possessing ultimately low intrinsic noise. Such amplifiers found important practical applications in space research.

Application of auxiliary radiation for population inversion in spin-system levels was the first realization of this principle of obtaining atomic states with negative temperature. This has led not only to creation of microwave masers but also stimulated further progress in quantum electronics – creation of laser.
EPR-spectroscopy is one of the most effective tools in studies of active media for solid-state lasers. In one's turn, development of quantum electronics significantly influenced further development of researches in EPR field, in particular for studies of relaxation processes in multi-level systems.

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