Optics and Spectroscopy, 2023, Vol. 131, No. 4

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Spin noise spectroscopy of rare-earth ions in crystals

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Received November 03, 2022
Revised November 03, 2022
Accepted November 17, 2022

Spin fluctuation spectroscopy (SNS) is a conceptually new version of magnetic resonance spectroscopy, experimentally demonstrated in 1981 and strongly developed in the last two decades. Atomic systems and semiconductors served as main objects of the SNS. It became possible to apply SNS to crystals with rare-earth impurities - classical objects of EPR spectroscopy and the subject of constant interest of P.P. Feofilov, only in recent years, due to specific combination of spectroscopic properties of rare-earth ions with characteristics of the stochastic signal formation in SNS. In this article, we consider the specific characteristics of application of SNS to crystals with rare-earth ions and briefly describe the results of experimental studies, which made it possible to significantly expand the scope of possibilities of this method.

Keywords: spin noise, magnetic resonance, rare-earth ions, birefringence, magnetooptics.

DOI: 10.61011/EOS.2023.04.56348.64-22

Introduction

In the 70s of the last century at the State Optical Institute named after S.I. Vavilov, on the initiative of P.P. Feofilov, work was organized on the polarization magneto-optics of crystals with rare-earth (RE) ions. As part of this line of research, an important question was raised about the sensitivity of polarimetric measurements, which determined the opportunities of detecting and diagnosing the properties of paramagnetic impurities. The solution of this problem of optical polarimetry showed that the limiting sensitivity of polarimetric measurements is limited by the shot noise of the photocurrent of the radiation detector and for real measurement conditions (using a laser light source) lies in the area $\sim 10^{-8}$ rad [1]. It is significant that this sensitivity on the magnitude scale was $\sim 10^{-8}$ from the saturated Faraday rotation (FR) of the impurity crystal. Since the value of the FR of a paramagnetic, as was known, is controlled by its magnetization, such a fantastic polarimetric sensitivity testified to the highest sensitivity of polarimetry to changes in its magnetization. Simultaneously, it was clear that the equilibrium magnetization of a paramagnetic sample is the result of the summation of the magnetic moments of a huge (but finite) number of constantly moving particles, and, therefore, should fluctuate. Moreover, the spectral and correlation properties of these fluctuations should carry information on the dynamics of the spin system. The question rested only on the sensitivity of measurements.

For the experimental observation of FR noise, we chose pairs of sodium atoms with lines of allowed optical transitions lying in a convenient visible area of the spectrum. The probe light of the dye laser was tuned to a wavelength near optical resonance, where the efficiency of conversion of magnetization into FR is maximum. Most of all we were interested in observation of FR noise in the direction transverse with respect to the magnetic field, where the noise spectrum should exhibit a resonant peak at the spin precession frequency (at the Larmor frequency). This paper, carried out in 1981 [2], demonstrated the practical opportunity of observing magnetic resonance in FR noise and laid the foundation for a new scientific direction — spin noise spectroscopy or spin fluctuation spectroscopy (SFS).

The first demonstration experiment [2], however, was carried out on a specially selected, exceptionally favorable object, and it seemed that the detected noise resonance was an interesting effect of fundamental physics, but could hardly serve as the basis for an experimental research method. Subsequently , the assessment was carried out that showed the apparent futility of applying the SFS method to solid-state systems. A parameter was introduced for assessment, called the FR cross section and numerically equal to the angle of rotation per unit length in terms of the unit spin density [3]. It turned out that while the value of this parameter for an alkali metal atom is on the order of $10^{-12}\,\mathrm{rad\,cm^2}$, for a n-GaAs semiconductor crystal this parameter is $10^{-15}\,\mathrm{rad\,cm^2}$, and for a dielectric crystal with a rare-earth impurity ion, it is another 4 orders of magnitude smaller ($\sim 10^{-19}\,\mathrm{rad\,cm^2}$) [4]. Nevertheless, at the beginning of this century, SFS was successfully applied to observe the spin resonance signal in the FR noise of semiconductors [5–7]. The key to solving this experimental problem was the replacement of a scanning-type spectrum analyzer with a Fourier spectrum analyzer. As a result, the sensitivity of the method was increased by more than two orders of magnitude, and at present the ground achievements of the SFS are related to the study of semiconductor systems [8–10].

It has been manageable to apply SFS to classical objects of EPR spectroscopy — impurity dielectrics — only in recent years. The noise signal amplification resource in this case was provided by the specifics of its formation under conditions of resonant sounding of the medium. The expansion of the range of SFS objects to include crystals with RE ions allowed to pose and solve a number of interesting problems related to the detection of noise in systems with heterogeneous broadening, in optically anisotropic media, and in crystals with anisotropic centers. The results of these studies, which are logically related to the successful application of spin noise spectroscopy to RE ions in crystals, are the subject of the present paper.

Spin noise on *f–f*-transitions of RE ions in crystals

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In the optical spectra of RE ions in crystals, as is known, transitions of two types are significantly different: allowed interconfigurational (*f–d*) transitions and weak intraconfigurational (*f–f*) parity-forbidden transitions (Fig. 1). Transitions of the first type are characterized by broad uniformly broadened absorption bands (which lie in the visible area of the spectrum for a number of divalent RE ions) and often by strong magneto-optical activity. Transitions of the second type are characterized by narrow, relatively weak absorption lines and low magneto-optical activity. Therefore, initially it seemed that the maximum FR noise would be observed where the FR itself is maximum, i.e. in the area of *f–d*-transitions on divalent RE ions. However, simple physical considerations and the assessments carried out have shown that the expected noise signal in magnitude lies significantly below the threshold of available polarimetric sensitivity. The subject matter was that high values of the FR of the impurity crystal in the area of the $f-d$ transition were achieved by a large number of ions, and not by large values of their individual contributions to the Faraday effect.

To solve this experimental problem, we turned to the results of studies of semiconductor systems with strong heterogeneous broadening — ensembles of quantum dots [11], where a paradoxical fact was discovered: the maximum signal in the optical power spectrum of the FR noise was observed at the wavelength , where the regular Faraday effect becomes zero. The theoretical analysis of the problem showed that, in the case of resonant probing of an optical transition with monochromatic light, the value of the spin noise signal depends significantly on the degree of heterogeneous broadening of the transition and cannot be correctly estimated from the FR cross section. Moreover, it turned out that as the ratio of the heterogeneous width of the optical transition to the homogeneous width increases, the noise power of the FR (assuming the linearity of the optical system) should experience an almost unlimited growth.

This effect of amplifying spin noise has a simple qualitative explanation. In linear optics, the absorption spectrum of an optical transition is known to be independent of the spectral width of the probe light (as long as it is small compared to the line width). In noise spectroscopy, this is generally not the case. In case of an heterogeneously broadened optical transition, as the spectral width of the probe light narrows, the absorption does not really change, but the number of fluctuating centers (optical oscillators, spins) contributing to this absorption decreases, and the relative fluctuation of the number of particles correspondingly increases. This continues until the spectral width of the probe light is equal to the uniform width of the optical transition line. At this moment, the noise power amplification factor will be approximately equal to the ratio of the heterogeneous width of the optical transition to the homogeneous one.

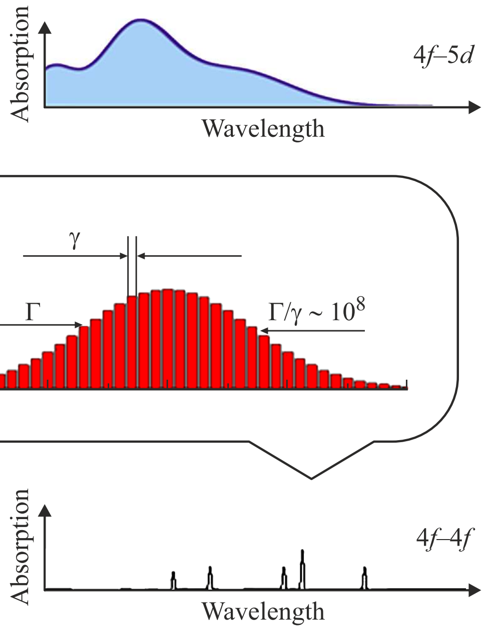

Figure 1. Schematic representation of two types of optical transitions of RE ions in crystals. Interconfigurational transitions (*4f–5d*), usually located in the short-wavelength part of the spectrum, are distinguished by broad, strong, uniformly broadened absorption bands, while longer-wavelength intraconfigurational transitions (*4f–4f*) are characterized by narrow weak lines with low magneto-optical activity . The heterogeneous width of these transitions (Γ), however, can exceed the uniform width (γ) by many orders of magnitude.

Taking into account this effect „, the unpromising" intraconfigurational transitions of RE ions appeared to us to be much more interesting. Th widths of „the narrow " lines of these transitions lie in the range $1-10$ GHz, while their uniform widths can reach fractions of a kHz [12,13], and the mentioned spin noise amplification factor can reach $6-7$ orders of magnitude, which greatly exceeds the potential signal loss associated with the transition from allowed *f–d*-transitions to forbidden transitions *f–f*.

All these considerations were confirmed in a series of experiments that we carried out [14]. A ring titanium-sapphire laser with a linewidth not exceeding 1 MHz was used as a source of probe radiation. The objects of study were cubic crystals of the fluorite type, activated by trivalent

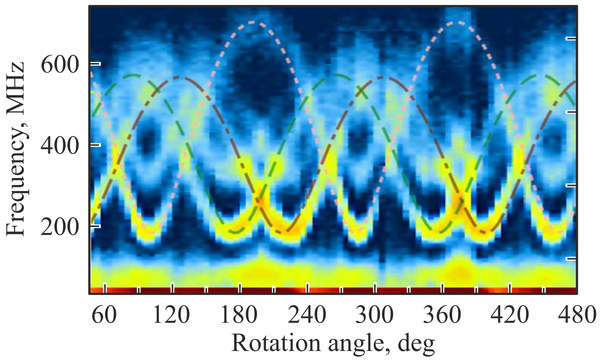

Figure 2. Angular dependence of the spin noise spectrum of the crystal CaF_2-Nd^{3+} (0.1 mol.%), obtained by rotating the magnetic field generated by a permanent magnet.

neodymium and ytterbium ions, the optical transitions of which fell into the area of laser tuning. The wavelength of the laser source was tuned to resonance with one of the *f–f* transitions, where the spin noise amplification effect for the heterogeneously broadened transition should be maximum. The low temperature of the sample ($\sim$5 K) ensured a small uniform width of the optical transition, essential for observing spin noise. As it was expected, the spin noise signals on different spectral lines of impurity ions differed significantly in magnitude, which we attribute to the difference in the uniform widths of the lines of the corresponding transitions. A detailed description of the measurement results is given in the article [14].

Invariants of spin noise spectra in cubic crystals with anisotropic centers

One of the methodological features of SFS, which distinguishes it from standard EPR spectroscopy, is the panoramic nature of the recorded spectra — at each fixed field value, accessible resonances of all centers associated with a given optical transition are simultaneously observed. In addition, spin noise measurements are carried out in the range of relatively low frequencies and, accordingly, in relatively small magnetic fields, which can be created by compact permanent magnets located outside the low-temperature cryostat. These methodological features of the SFS were used to study the orientational dependences of the spin noise spectra in crystals with anisotropic centers [15]. In contrast to the EPR technique of sample rotation in a magnetic field, we used a rotating magnetic field, which was created by a rotating permanent magnet located outside the cryostat. An example of such a record obtained in the study of an CaF_2 crystal with Nd^{3+} tetragonal centers is shown in Fig. 2.

It is easy to see that in the high-temperature approximation, which complies with the conditions of the described experiments, the frequency of each resonance of the noise spectrum reflects numerically the contribution of the corresponding group of centers to the total crystal magnetization. Taking into account the magnetic isotropy of a cubic crystal, this fact imposes certain conditions on the set of frequencies (or the set of effective g factors) of resonances of all magnetically nonequivalent centers in a cubic crystal. It was shown in [15] that under a rotating magnetic field of a fixed value, the sum of squared resonance frequencies (or the sum of squares of the corresponding effective g-factors) is invariant. In standard EPR spectroscopy, where the measurements are carried out at a fixed frequency of the RF generator, this invariant is represented by the sum of the inverse squares of the resonant fields.

The obtained simple invariant relations can be useful in the analysis of the magnetic resonance spectra of multicenter systems of cubic crystals, as well as uniaxial crystals in the plane of their magnetic isotropy.

SFS and the nonlinear Faraday effect in crystals with RE ions

The above results show that the successful application of SFS to crystals with RE ions became possible only due to the spectral narrowness of the lines of individual *f–f* transitions against the background of large values of their heterogeneous widths. Our studies of crystals activated by Nd^{3+} showed that there is no spin noise at all available *f–f* transitions. This result seems quite natural if we take into account the potential difference in the dipole moments of the transitions, as well as the fact that the disintegration rate of various excited states (and hence the uniform linewidth) can be controlled to different degrees by nonradiative relaxation processes and differ significantly for transitions between different splitting components multiplets by the crystal field.

In the paper [16] it was shown that in order to establish the opportunity of applying the SFS method to a particular transition, it is not at all essential to carry out direct noise measurements on it. As the power density of the probe beam increases, a dip is burned in the absorption spectrum of the heterogeneously broadened transition, the width of which (in the initial stages of saturation) approximately corresponds to the uniform linewidth. Under these conditions, the diamagnetic contribution is determined by the Zeeman splitting of levels not on the scale of the width of the optical transition line, but on the scale of the width of the burnt dip. The resulting additional contribution to the resonant Faraday effect, firstly, exhibits a dependence on light intensity (*nonlinear* Faraday effect) [17], and, secondly, it can exceed *linear* FR observed under conditions of non-perturbing probing of the medium. Meanwhile, the corresponding FR amplification factor (as well as the spin noise amplification factor mentioned above) is approximately equal to the ratio of the heterogeneous linewidth to the homogeneous one.

The described effect „of the giant enhancement of the FW“, experimentally demonstrated on crystals with RE ions [16], not only offers a method for diagnosing heterogeneously broadened optical transitions, but also establishes a connection between the effects of nonlinear optics and spin noise spectroscopy, assuming optical nonlinearity of the medium.

Application of SFS to birefringent media

Initially, it was assumed that SFS or FR noise spectroscopy as a polarization technique is applicable only to optically isotropic paramagnetics, where the probe light polarization is not significantly distorted by the intrinsic birefringence of the medium. Strong linear birefringence, as is well known, makes the regular FR of a medium practically unmeasurable. For this reason, it was difficult to assume that the opportunity of measuring the noise of this immeasurable quantity would still be preserved. However, as shown in a recent paper [18], this is true.

Despite the simplicity of the problem, its rigorous solution turns out to be rather complicated. This effect can be qualitatively explained, for example, as follows. Polarized light, propagating in a birefringent medium, passes through a sequence of half-wave phase plates. Meanwhile, the angle of rotation of the polarization plane, acquired in a selected area of the medium, after passing through the half-wave plate, changes sign, as a result of which the regular FR is suppressed. The FR noise signal is not suppressed, since it has no definite sign, and the noise contributions of individual sections of the medium are always added statistically.

The picture of the evolution of the polarized state of light in an anisotropic medium, as well as the picture of the suppression of gyration in it, are clearly described as the precession of the quasi-spin vector in the Poincare sphere, where the linear and circular anisotropy of the medium are represented by the mutually orthogonal components of the magnetic field acting on the quasi-spin [4,19] . In this model, the gyrotropy of the medium in the presence of dominant linear birefringence leads to only a slight change in the effective magnetic field, which has practically no effect on the polarization evolution of light. From this visual picture, it can be understood that a spatially uncorrelated gyration noise signal, in contrast to regular gyration, can accumulate as it propagates in a medium.

Seriously, the calculations and measurements carried out on anisotropic crystals with RE ions have shown that the birefringence of the crystal has almost no effect on the magnitude of the measured noise signal [18]. Moreover, it turned out that the signal also practically does not depend on the azimuth of the probe light polarization plane with respect to the crystal anisotropy axes. Such „isotropy" of anisotropic crystals is of great interest from the point of view of SFS practice — the application of this polarization method to an anisotropic crystal does not require the orientation of the crystal in the light beam.

SFS of anisotropic paramagnetic centers peculiarities

When studying the orientational dependences of the spin noise spectra of crystals with anisotropic centers, when the measurement geometry was constantly changing during the rotation of the magnetic field, successively changing the Faraday geometry to the Focht geometry and vice versa, we paid attention to the fact that the intensities of the resonance peaks remain practically unchanged in this case and in Faraday geometries do not become zero. The explanation for this phenomenon seemed fairly obvious to us. The magnetic field directed along the light beam turns out to be arbitrarily oriented with respect to the axes of the anisotropic center. Because of its magnetic anisotropy, the center „sees" different field components differently. As a result, the effective magnetic field acting on it turns out to be deviated from the external one, the Faraday geometry of the experiment is violated, and the observation of precession resonance in nominally Faraday geometry becomes possible.

Such reasoning qualitatively leads to a correct conclusion, but, strictly speaking, is incorrect. As the results of a more rigorous theoretical consideration of this problem showed, the subject of the incorrectness of this reasoning lies in the unfairness of the generally accepted statement (often referred to as the Van Vleck theorem) that the value of the paramagnetic contribution to the FR directly reflects the magnetization of the paramagnetics. One of the approximations of the Van Vleck theorem, which was undoubtedly violated in our resonance studies of RE ions, was a large detuning of the probe light frequency from optical resonance.

Our experimental measurements of the spin noise spectra in crystals with anisotropic centers confirmed that, in the general case, in such systems, the difference between the Vocht geometry and the Faraday geometry is erased. As a result, the noise „of the longitudinal" magnetization, centered at zero frequency, and the magnetic resonance noise „of the transverse" magnetization, can be observed in such systems in arbitrary geometry of the experiment. Let us note that the very fact of observing spin noise resonances in Faraday geometry may indicate the presence of anisotropic paramagnetic centers and thus be considered as a way to reveal the hidden anisotropy of isotropic media [20].

Conclusions

The development of spin fluctuation spectroscopy in recent years has significantly expanded the range of objects of study of this technique both at the expense of RE paramagnetics and at the expense of previously inaccessible media with high linear birefringence. The latter circumstance opens up new possibilities for applying SFS to topical materials of modern photonics, such as halide perovskites, with their unique magneto-optical properties [21]. The strong selectivity of the EPR noise technique over the optical channel makes it a unique tool for studying multicenter paramagnetics with arbitrary optical anisotropy. The SFS peculiarities associated with the absence of a radio frequency excitation channel and not implying magnetic polarization of the medium, together with its well-known unique capabilities [7,22], simplify this technique and additionally attractive. To date, the SFS technique has included almost all relevant magnetically dilute paramagnetics among its objects, and there is every reason to count on the further development of this scientific direction.

Funding

The author is grateful to the Russian Science Foundation (grant № 21-72-10021) for supporting the experimental studies described in Sections 5 and 6 of the article. Preparation of samples for research was carried out with the support of St. Petersburg State University (grant No. 94030557). The author's work under Megagrant 075-15-2022-1112 of the Ministry of Science and Higher Education of the Russian Federation allowed to significantly expand the prospects for applying SFS to semiconductor systems with strong spin-orbit interaction noted in the article.

Conflict of interest

The author declares that he has no conflict of interest.

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Translated by E.Potapova