USE OF LASERS TO STUDY MAGNETIC RESONANCE AND MAGNETIC RELAXATION

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Optical methods of recording ESR, which were developed in the early 1950s to record magnetic resonance of excited atoms, are extensively used at present in investigations of ESR of the ground and excited states of atoms and paramagnetic centers in condensed media [1]. Attention is called in the present communication to additional capabilities of optical ESR and of paramagnetic relaxation methods, which are realizable through the use of laser sources.

I. Introduction

There are two known approaches [2] to the problem of recording electron spin resonance: 1. the approach based on recording the resonant change in the state of the microwave field that induces the ESR (this approach, discovered by Zavoiskii, is the contemporary basis of traditional microwave spectroscopy of condensed media); 2. the approach in which the changes due to saturation of the magnetic transitions of some parameter of the medium are recorded. This trend, historically traceable to the method of Rabi beams, started to be intensively developed following the work by Kastler and Brossel on optical recording of ESR in gases. The adoption of these ideas in solid-state physics led to extensive research into optical orientation and spin relaxation of carriers in semiconductors, as well as to the development of an arsenal of combined optical and microwave methods of investigation of paramagnetic centers in semiconductors and in dielectrics.

For gases and condensed media, the efforts of the researchers were primarily aimed at the study of excited centers, whose low density precludes their investigation by the usual ESR methods. This difficulty could be overcome by turning to optical methods. For example, isolation of fluorescence of excited centers permits selective determination of changes of the intensity or of the polarization of their optical emission due to induced change of their magnetization. High sensitivity is achieved in this case mainly by changing from the extremely weak relative absorption of the microwave field to the much larger changes of the light intensity, reaching in the limit 100%.

Notwithstanding the importance of the study of excited centers, of principal interest to physicists, biologists, engineers, and technologists is ESR of the ground states of paramagnetic centers, which provides important and diverse information on the structure of the medium.

To study paramagnetic centers in the ground state, various optical effects are used, viz., magnetocircular dichroism and magnetocircular birefringence (the Faraday effect), which are based on the dependence of the optical axial anisotropy on the degree of magnetization of the medium, and the effect of self-absorption of resonant radiation, which is sensitive to the distribution of the center populations over the ground state populations. The latter effect is used in those rare cases when the magnetic energy structure of the center is spectrally resolved in the optical transitions.

The particular optical procedure chosen depends on the actual investigated objects, and the attainable sensitivity can vary in a wide range. Fortuitous coincidences in the search for a successful experimental situation influenced, to a considerable degree, the opinion held by microwave spectroscopy specialists that the optical methods of ESR constitute a variegated set of clever tricks. In our opinion, this attitude should change, in view of recent successes in this field, due to the use of lasers in conjunction with the Faraday technique. It became possible to develop on this basis a simple and quite sensitive ESR spectrometer whose...
advantages are great versatility both with respect to the objects investigated and in the sense of flexibility of the operating regimes, which permitted wide-band resonant as well as nonresonant investigations of paramagnetism.

2. Registration of ESR by the Faraday Effect

The Faraday effect, meaning the rotation of the polarization plane of light passing through a medium along a magnetic field, contains, in the case of a paramagnetic medium, a contribution that is determined by the magnetization of the medium, i.e., by the difference between the populations of the sublevels of the magnetic splitting of the paramagnetic centers. Therefore, the redistribution of the populations due to the action, say, of a field at resonant frequencies, changes the orientation of the polarization plane of the light passing through the probed medium. The Faraday effect is a reflection of the difference between the refractive indices of the medium for two circular polarizations of the light. Therefore, its magnitude, as a function of the wavelength, behaves in accordance with the dispersion of the refraction, and later increases in the vicinity of the optical absorption bands of the paramagnetic centers. A fact of importance for purposes of optical recording of ESR is the fact that the refraction decreases much more slowly with increasing distance from the absorption band than the absorption itself. This makes it possible to record the paramagnetic Faraday rotation in the transparency region of the sample also far from the absorption bands. The feasibility of using the "tails" of the paramagnetic Faraday effect for sensitive registration of magnetization changes is obviously determined by the sensitivity of the polarimetric procedure. We shall show below that the polarimetric sensitivity attainable by using laser sources makes it possible to preserve a high "magnetometric" sensitivity in the optical-registration channel far from optical resonances.

In the transparency region, a shift, small compared with the frequency distance to the absorption band, in the frequency of the probing light, has little influence on the magnitude of the effect, i.e., the Faraday technique is spectrally much less selective in the transparency region. It is therefore possible to use successfully in the Faraday ESR spectrometer a light source in the form of a laser with one or several fixed wavelengths.

The main features and advantages of a laser ESR spectrometer are common to all optical ESR methods and stem from the complete isolation of the signal (optical) channel from the high-frequency field acting on the spin system. Let us list the consequences of this circumstance.

1. The restrictions imposed on the microwave power by saturation of the microwave transitions or by the overloading of the detector are lifted since, in optical detection, the ESR signal does not depend explicitly on the degree of absorption of the microwave power by the sample. This is particularly important in investigations of forbidden microwave transitions. Examples of realization of this advantage are given in [3], where optical registration revealed hitherto unknown types of rare-earth activator centers for BaF₂ crystals.

2. The sensitivity of an optical ESR spectrometer does not depend on the Q of the microwave resonator, the presence of which is not at all obligatory. It is only necessary to ensure the required intensity of the alternating field applied to the sample. This can be done with a broadband inductor. The apparatus ceases thereby to be tied in with the fixed resonance frequency, thereby greatly increasing the flexibility of the ESR method. By way of illustration of this situation, Fig. 1 shows a family of plots of optical ESR signals of a Tm³⁺ ion in a CaF₂ matrix in the frequency range 150-1200 MHz. Figure 2 shows the energy sublevel scheme of the ground state of the ion, and supplements the presented spectra [4]. Since no high-Q resonator is necessary, the requirements on the frequency stability of the microwave fields are relaxed and the restrictions are lifted on the admissible microwave levels in the samples; this is particularly important when working with aqueous solutions.

3. An important methodological feature of the optical ESR spectrometer is the possibility of amplitude-modulating the microwave field. This permits direct registration of the resonance line, rather than of its derivatives, as in the standard method of field modulation. This eliminates the usual signal losses due to the requirement that the amplitude modulation be small compared with the line width. The use of a laser ESR spectrometer to study very broad ESR lines in glasses was demonstrated in [3].

4. Optical registration of ESR offers an additional possibility of optical selection of the ESR signal for centers of various types. Retuning the wavelength of the probing light