Multifrequency spectroscopy of defects in complex oxides

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The typical output of the one-frequency methods is an image with a space resolution of the order of the used wavelength. Such images contain direct evidence about the space structure of a lattice or macroscopic defects; however, they are not very helpful for the study of the internal structure of the atomic-size defects. Measurements which use sweeping of electromagnetic wave frequency or sweeping of an external parameter furnish spectra or dependencies of measured characteristics on the swept quantity. The spectra contain indispensable information about energetic characteristics of interactions of intrinsic and extrinsic defects with the lattice ions. Different frequencies in very wide region have to be used for the study of these interactions (multifrequency spectroscopy). An application of this new approach to defects in lithium niobate allowed to determine characteristics of various interactions with magnitudes from $10^4$ to $10^{16}$ Hz, and to correlate them with definite models of the defects.

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1 Introduction

The usual scheme of many methods for material investigation includes an emitter of electromagnetic waves with the frequency $\nu$ and detectors for the registration of transmitted or reflected waves. Examples of this scheme are various microscopes. The typical output of the one-frequency methods is an image with a space resolution of about the used wavelength $\lambda = c/\nu$. In order to increase the resolution up to the atomic level a decrease of the wavelength up to 0.1 nm or less is used (X- and $\gamma$-rays, synchrotron, electron or neutron irradiation). The observed image (or diffraction picture) can be easily interpreted in many cases. However, in some cases the images should be simulated using some characteristics of lattice ions and models of possible lattice defects (Fig. 1) and compared with the observed ones [1]. The one-frequency methods are very successful for the study of the lattice structure and its transformation at phase transitions, for the determination of the sizes and geometry of macroscopic lattice imperfections like domains, twins etc. Sometimes they allow us to investigate intrinsic point defects if their concentration is rather high. This information is very helpful; however, often it is not sufficient for tailoring physical properties of materials.

Another approach is a measurement that uses sweeping of the frequency or sweeping of an external parameter: electric or magnetic field, pressure, temperature etc. The typical result of such a measurement is a spectrum or a dependence of measured characteristic on the sweeping parameter (but not an image). The spectra do not contain direct evidence about the space structure of a lattice or defects. Therefore, an interpretation of these spectra is not as obvious as the image interpretation. However, they contain very
important information about the energetic characteristics of interactions of lattice ions and intrinsic and extrinsic defects with the lattice. Due to the fast development of acquisition technique the registration of a signal change under sweeping of two or even three different external parameters (two- and three-dimensional spectroscopy) is now possible.

2 Do we really need a multifrequency spectroscopy?

A system of defects in a material can be characterized by many interactions of various kinds. For point lattice defects (like impurity ions and their charge compensators, antisite ions and vacancies, radiation defects etc) the interactions include at least: Coulomb interactions of electrons at an ion with their nucleus, Coulomb interactions of the electrons with the surrounding ions (crystal field), spin–orbit interactions, exchange interactions of electrons, hyperfine interactions of electron and nuclear spins, interactions of nuclear quadrupole moments with gradients of crystal electric fields. These interactions have very different energies or frequencies: from $10^3$ Hz up to $10^{16}$ Hz (Fig. 2). Therefore, monochromatic measurements or even investigations with the help of frequencies in a restricted range (for instance, with the help of visible light) can give information about one or two interactions only. In order to get a more or less complete set of characteristics multifrequency spectroscopy has to be used. It should involve several complementary methods like optical spectroscopy (IR, visible and UV), microwave and radio-frequency spectroscopy: electron paramagnetic resonance (EPR [2]), nuclear magnetic resonance (NMR [3]), electron nuclear double resonance (ENDOR [4]), nuclear quadrupole resonance and so on.
3 Strategy of multifrequency investigations

In reality, optical, microwave and radiofrequencies give us a huge array of characteristics of Coulomb and exchange and hyperfine interactions. This is a very good basis for understanding the nature and models of the defects. Therefore, the NMR, ENDOR, EPR, optical detection of magnetic resonance, and simultaneous EPR – optical spectroscopy [5] should be the basic methods for multifrequency research. Since magnetic resonance is observed for magnetic defects only, some additional procedures can also be used if necessary to obtain information about non-magnetic defects (for instance, defect recharging or excitation to a paramagnetic state).

No spectral line has an initial label. This is valid for optical absorption and luminescence and for NMR, EPR and ENDOR as well. However, the values of magnetic moments for all nuclei and the electron spins for many ions are well known and collected in tables (see, for instance, yearly Bruker Almanc). We can easily use these spin labels for the evaluation and interpretation of obtained spectra. Another great advantage of the magnetic spectroscopy is the possibility to study dependencies of observed spectra on the mutual orientation of a crystal and magnetic field (so called angular dependencies [2, 4]). They give us conclusive proof of defect symmetry. For instance, if the observed spectrum does not change at the rotation of magnetic field in one plane, but has angular dependence in another plane, we deal with an axial center.

Therefore, an optimal strategy for the multifrequency investigation of paramagnetic defects in a crystal is the following. At the first step the EPR/ENDOR spectra and their angular dependencies are studied. The EPR data allow us to determine the kind and charge state of the paramagnetic defect, symmetry of the lattice site, the value of crystal field at this site and so on. The ENDOR data allow us to determine surrounding nuclei, i.e. defect location, the position and kind of charge compensator, the distortion around the defect, the distribution of the electron wave function density. This information is often sufficient for the simulation of observed EPR/ENDOR spectra and for the construction of reliable models of defects studied [6, 7]. At the next step these models can be used for the interpretation of optical absorption and luminescence spectra (Fig. 3).
4 Application of multifrequency spectroscopy to the chromium in lithium niobate

In order to illustrate the efficiency of multifrequency spectroscopy we consider results of our study of lithium niobate crystals doped with chromium. A detailed analysis of the observed EPR/ENDOR spectra and their angular dependences has shown that there are two families of chromium centers in LiNbO₃. In the first family the Cr³⁺ ion substitutes for Li and has a cation vacancy as a charge compensator in the neighbourhood, whereas in the second family the Cr³⁺ ion substitutes for Nb⁵⁺, and a deficit of positive charge is compensated by H⁺ ions (protons) or by interstitial Li⁺ ions in the neighbourhood. Based on the ENDOR data the EPR lines with a small splitting were attributed to CrNb, and with a large splitting to CrLi. Since the ratio of the intensities of the EPR lines for these centers correlates with those of optical bands, these bands were also assigned: CrLi centers give the main contribution to a band at 660 nm, whereas CrNb to a band at 510 nm (Fig. 3).

Another example, which illustrates the necessity of multifrequency spectroscopy, is the studies of crystals with such high dopant concentration that pair complexes of impurities appear. The pairs with exchange interaction $J$ of about 300 cm⁻¹ were registered in optical spectra [8–10]. Several lines in the EPR spectra [11–13] were also related to pair complexes, however with an exchange interaction, which is comparable with the energy of microwave quanta ($J \sim 1.5$ cm⁻¹). There is no contradiction in these data. The peaks observed in the optical spectra belong to the closest CrLi–CrNb pairs (this complex has axial symmetry), whereas the EPR lines belong to low-symmetry pairs consisting of two Cr ions substi-
tuting Li ions and one niobium vacancy for the charge compensation (Fig. 4). This means that the EPR and optical spectra allow us to get complementary information. Axial exchange pairs were also observed by the EPR at high temperatures; however, it is rather difficult to determine the parameter of the exchange interaction with spectroscopic accuracy using microwave frequencies.

The magnitudes of interactions, which we have determined for chromium in lithium niobate, cover a wide range (Table 1). Some of them were measured earlier with the help of various techniques; for examples, by optical absorption [14–18] and luminescence [19–22]. The different optical bands were labelled by α, β, γ, δ, ε, and related to a majority and a minority of chromium centers. The centers observed by the EPR [23–25] were assigned to the site with axial C₃ symmetry. However, three different sites have this symmetry in lithium niobate: Li site, Nb site and structural vacancy. The multifrequency approach allows us to correlate all data with definite models of the chromium centers conclusively.

Table 1  Characteristics of chromium centers in LiNbO₃.

<table>
<thead>
<tr>
<th>interaction</th>
<th>order of magnitude, Hz</th>
<th>comment</th>
<th>technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>optical band</td>
<td></td>
<td>CrLi, CrNb</td>
<td>optical</td>
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<td>(screened coulomb)</td>
<td>4.5 × 10¹⁵</td>
<td>CrLi, CrNb</td>
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<td>exchange</td>
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<td>emission, EPR</td>
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<td>9 × 10¹²</td>
<td>CrLi – CrLi – vNb</td>
<td>EPR</td>
</tr>
<tr>
<td></td>
<td>3 × 10¹⁰</td>
<td>CrLi – CrLi – vNb</td>
<td></td>
</tr>
<tr>
<td>crystal field</td>
<td></td>
<td>CrLi, CrNb</td>
<td></td>
</tr>
<tr>
<td>(fine structure)</td>
<td>1.2 × 10¹⁰</td>
<td>CrLi, CrNb</td>
<td>EPR</td>
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<tr>
<td></td>
<td>6.4 × 10⁹</td>
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<tr>
<td>hyperfine and</td>
<td></td>
<td>own ⁵⁵Cr nucleus</td>
<td></td>
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<td>superhyperfine</td>
<td>5 × 10⁷</td>
<td>¹H, Cr⁹⁵</td>
<td>ENDOR</td>
</tr>
<tr>
<td></td>
<td>6 ÷ 10 × 10⁶</td>
<td>⁷Li, Cr⁹⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 ÷ 12 × 10⁶</td>
<td>⁸³Nb, CrLi</td>
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<td></td>
<td>3 ÷ 8 × 10⁶</td>
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<td>NMR, ENDOR</td>
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<tr>
<td>quadrupole</td>
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<td>distant ⁸³Nb</td>
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<td></td>
<td>2 × 10⁷</td>
<td>distant ⁷Li</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 × 10⁶</td>
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5 Conclusions

Multifrequency spectroscopy (including EPR and ENDOR as well as simultaneous EPR and optical measurements) has exceptional power for the study of correlated complexes of intrinsic defects in undoped samples, the joint entering of impurities and charge compensating defects in doped crystals, the structures of different impurity centers in various materials. It is able yield reliable information about many very fine features of defects: defect recharging processes, reduction and oxidation processes.
microscopic instabilities and so on. The obtained characteristics of different interactions (i.e. a “passport” for each of the defects) can be used as cornerstones for theoretical calculations of defects.

It is very common that research groups use different techniques measuring various characteristics of a crystal with defects. However, it is often too difficult or even impossible to correlate these characteristics with the same defects. The multifrequency approach and simultaneous EPR/ENDOR/optical spectroscopy should help us to avoid false judgments about defects and their properties, and to construct a complete picture of defect interactions.

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References