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EPR and dielectric spectroscopy of reorienting Cr^{3+}– Li^{+} pair centres in $Li_2Ge_7O_{15}$ crystal

M.D.Volnianskii, M.P.Trubitsyn, Yahia A.H.Obaidat

Department of the solid state physics, Dnipropetrovsk National University,
13 Naukova Str., Dnipropetrovsk 49050, Ukraine

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Earlier it has been shown that in the lithium heptagermanate $Li_2Ge_7O_{15}$ structure the chromium doping ions substitute the germanium hosts and create Cr^{3+}– Li^{+} pair centres. In the paper EPR and dielectric spectra of $Li_2Ge_7O_{15}$:Cr^{3+} crystal are studied in the temperature range $300 \div 500$ K. The thermally activated reorientation of Cr^{3+}– Li^{+} pairs has been detected through EPR line width broadening and dielectric relaxation.

Key words: *impurity ions, electron paramagnetic resonance, dielectric loss and relaxation*

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1. Introduction

It is known that Cr^{3+} doping ions in the structure of $Li_2Ge_7O_{15}$ (LGO) crystal substitute the Ge^{4+} host ions within oxygen octahedral complexes [1]. Incorporation of chromium ions into oxygen octahedra changes the local symmetry of the lattice site from monoclinic C_2 group to triclinic C_1 group. The local symmetry lowering is attributed to the effect of the additional defect compensating the charge misfit of Cr^{3+} ion at the Ge^{4+} site. Taking into account a weak coupling of lithium ions with the germanium – oxygen lattice framework [2], the interstitial Li^{+} is considered to be the most probable charge compensating defect, located within the structural cavity near the octahedral CrO_6 complex. Subsequent measurements of optical spectra have confirmed the model of Cr^{3+}– Li^{+} pair centres in the LGO crystal structure [3,4].

The available data make it possible to assume that electric dipole moments of Cr^{3+}– Li^{+} pairs are directed along the crystal axis a. Interstitial Li^{+} ions locally break the symmetry axis $C_2 \| b$ of the sites within the oxygen octahedral complexes [2]. As a result, there are two equivalent configurations of the pair centres which are conjugated by broken C_2 axis and have dipole moments with opposite orientations. It may be assumed that pair centres can reorient due to thermal activation. Reorientation of the pair centres should be accompanied by: i) shortening of the configuration life time and ii) switching of defect dipole moments.

The paper is devoted to the detection of thermally activated Cr^{3+}– Li^{+} reorientation in LGO:Cr^{3+} crystal through measurements of EPR spectra and dielectric permittivity.

2. EPR lines width broadening

Angular variations of LGO:Cr^{3+} EPR spectra [1,5] have shown that for arbitrary orientations of static magnetic field B with respect to the crystal axes there are four ($k_m = 4$) conjugated spectra of triclinic symmetry C_1. For magnetic field B rotating in the main crystal planes two structurally equivalent Cr^{3+} spectra are registered. If Cr^{3+} centres kept the monoclinic local symmetry C_2 of the perfect lattice sites, then the magnetic multiplicity of the spectrum would be $k_m = 2$ with unique direction along axis b [6]. In this case, for a magnetic field rotating in (ab) and (bc) planes one spectrum would be observed, whereas in (ac) plane two conjugated spectra would be detected. Therefore, doubling of the spectra in (ab) and (bc) planes results from lowering of the positional symmetry $C_2 \longrightarrow C_1$ due to the formation of Cr^{3+}– Li^{+} pair centres. Assuming that at high temperatures the probability of reorientation between equivalent states should increase, it may be supposed that in (ab) and (bc) planes EPR spectra should broaden on heating [7]. It may be expected that a fast enough reorientation between equivalent configurations should average the local distortions produced by pair centres, and effectively restore point symmetry C_2 of the perfect lattice site.

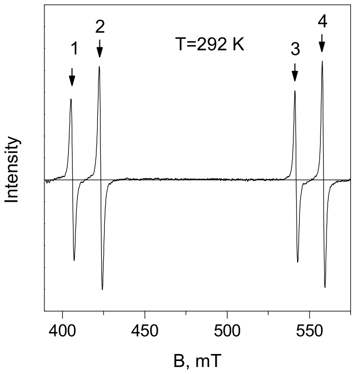

Figure 1. Fragment of LGO:Cr^{3+} EPR spectrum: four conjugated lines corresponding to electronic transition $|M_S| = 1/2 \longleftrightarrow 3/2$.

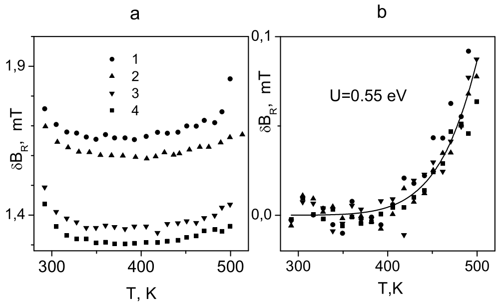

Figure 2. Temperature dependencies of the line width of the spectral components depicted in the figure 1: a) the total peak-to-peak line width; b) the line width, contributed by Cr^{3+}– Li^{+} centres reorientation.

At low enough temperatures the so-called slow reorientation limit is valid [7]. The spectra from equivalent configurations are observed separately. EPR lines broaden on heating and the line width is inversely proportional to the life time τ' of the equivalent configurations

$$\delta B = \delta B_0 + \frac{h}{g\beta} \cdot \frac{1}{2\sqrt{3}\pi}(\tau')^{-1}, \qquad (1)$$

where δB_0 is the background line width contributed by all other mechanisms except for the pair centres reorientation, h is Planck constant, g is the spectroscopic factor, β is Bohr magneton, the life time τ' and relaxation rate $(\tau)^{-1}$ exponentially depend on the inverse temperature $(\tau'/2) = \tau = \tau_0 \exp(U/kT)$, $(\tau_0)^{-1}$ is frequency of oscillations near potential minima, U is activation energy, k is Boltzmann constant.

EPR spectra of LGO:Cr^{3+} were measured using a conventional X-band spectrometer. The temperature of the samples was regulated by a standard gas flow cryostat. To detect the assumed local kinetics, the magnetic field B was rotated from c axis to b axis by 26^0 and then tilted from (bc) plane by $\approx 0.8^0$. For such an orientation, all four conjugated spectra are distinctly resolved. The group of conjugated EPR lines corresponding to the electronic transition $|M_S| = 1/2 \longleftrightarrow 3/2$ (figure 1) was measured in the temperature interval $290 \div 500$ K. The line shape was described by a Lorentzian, the temperature dependencies of the line width are depicted in figure 2a. For all components the studied linewidths demonstrate non-monotonous temperature dependencies $\delta B(T)$. The decrease of δB on heating in the interval $290 \div 380$ K is obviously connected with ferroelectric phase transition ($T_\mathrm{C} = 283.4$ K) which is accompanied by an EPR line width anomaly [5]. The anomalous line width broadening has been described by the Curie-Weiss law, and for the background line width in (1) the following expression was used

$$\delta B_0 = \delta B_0^0 + \frac{C_\mathrm{CW}}{T - T_\mathrm{C}}\,. \qquad (2)$$

The temperature dependence δB_0 in (2) being taken into account enables us to derive the line width contributed by the pair centres reorientation. The temperature dependencies of the line width originated from the pair centres dynamics are presented in figure 2b.

The oscillation frequency $(\tau_0)^{-1}$ was estimated from the Debye temperature which has a typical value of $\theta_\mathrm{D} \approx 200$ K for the crystals of germanate family [8]. The activation energy is estimated as $U = 0.55 \pm 0.05$ eV from the line width of the four components registered. Evidently, in the temperature interval studied the line width broadening is too small ($\sim 7\%$ from the background line width) and the activation energy is determined with low accuracy. Nevertheless, one can estimate in what temperature and frequency range the permittivity anomalies from Cr^{3+}– Li^{+} reorientation can be detected.

3. Dielectric relaxation of Cr^{3+}– Li^{+} pair centres

The permittivity of pure and Cr^{3+} doped (0.1 wt.) LGO crystals was measured using a bridge method in the temperature interval $300 \div 500$ K and frequency range $0.5 \div 10$ kHz. Dependencies of real ε' and imaginary ε'' parts of LGO:Cr^{3+} permittivity measured along a axis are plotted in figures 3a, b. There is a distinct $\varepsilon'(T)$ step-like anomaly and $\varepsilon''(T)$ maximum which shift to high temperature side with the increasing of measuring field frequency f. Along b and c axes the quantities ε' and ε'' of LGO:Cr^{3+} do not demonstrate any anomalies and slightly depend on temperature. For nominally pure LGO crystal, the real and imaginary parts of permittivity monotonously depend on temperature and do not show any anomalous features.

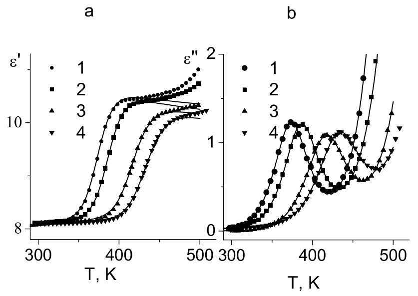

Figure 3. Temperature-frequency dependencies of a) real ε' and b) imaginary ε'' parts of LGO:Cr^{3+} permittivity, measured along a axis at the following frequencies f: 0.5 kHz (1); 1 kHz (2); 5 kHz (3); 10 kHz (4).

The anomalies of the LGO:Cr^{3+} permittivity are typical of a thermal polarization process [9]. The experimental data show that ε', ε'' anomalies are contributed by chromium dipole moments directed mainly along a axis. To determine the parameters of pairs centres reorientation, the real and imaginary parts of complex permittivity $\varepsilon^*(T)$ (figure 3) are described by means of the Debye model

$$\varepsilon^* = \varepsilon' - \mathrm{i}\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \mathrm{i}\omega\tau}, \tag{3}$$

where $\varepsilon_0 - \varepsilon_\infty = C/T$, C is Curie constant, ω is angular frequency of measuring field and $\tau = \tau_0 \exp(U/kT)$ is relaxation time.

Fitting of (3) to the experimental data was carried out for the imaginary part of permittivity, since processing of $\varepsilon''(T)$ maxima enables us to determine the parameters in (3) to a higher accuracy in comparison with less pronounced step-like $\varepsilon'(T)$ anomalies. At high temperatures the background component of $\varepsilon''(T)$ sufficiently increases as it may be described by the expression $\varepsilon''_{\mathrm{bgr}} = \varepsilon^0_{\mathrm{bgr}} + A\exp(-W/kT)$, where $\varepsilon^0_{\mathrm{bgr}}$ is the temperature independent part and $W = 0.85$ eV is the activation energy for the exponential growth of the background component. The dependencies calculated by using (3) are shown in figure 3 by solid lines, the parameters used are

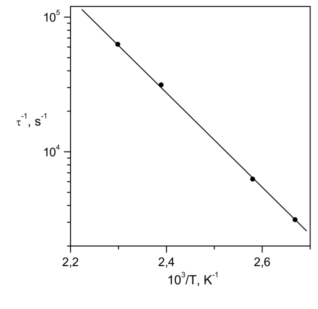

Figure 4. Reorientation rate of Cr^{3+}– Li^{+} pair centres vs inverse temperature.

$$\begin{aligned} \varepsilon_\infty &= 7.59 \pm 0.017, & C &= 907 \pm 14 \text{ K}, \\ \tau_0 &= (4.5 \pm 2)\cdot 10^{-13} \text{ s}, & U &= 0.66 \pm 0.02 \text{ eV}. \end{aligned} \tag{4}$$

The comparison of the measured data and the calculated dependencies reveals that the Debye model makes it possible to describe the experimental results. The temperature dependence of the relaxation rate τ^{-1}, obtained from $\varepsilon''(T)$, may be described by the Arrhenius law with good accuracy (figure 4).

It may be noted that the activation energy U determined from the dielectric measurements (4) is close enough to the value (0.55 ± 0.05 eV), estimated from the EPR spectra. The frequency $(\tau_0)^{-1}$ (4) agrees well with independent measurements of the Debye temperature $\theta_{\mathrm{D}} \approx 200$ K [8].

4. Conclusions

Investigations of EPR and permittivity spectra have made it possible to detect the thermally activated reorientation of Cr^{3+}– Li^{+} pair centres in LGO crystal. The reorientation of Cr^{3+}– Li^{+} pairs leads to a temperature EPR line width broadening and results in relaxation anomalies of the dielectric permittivity.

The reorientation of the pair centres is apparently realized by the hopping of interstitial Li^{+} ions through the channels of LGO structure. It is obvious that the spatial location of Cr^{3+} ions is fixed within the oxygen octahedral complexes.

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ЕПР і діелектрична спектроскопія Cr^{3+}– Li^{+} парних центрів, що реорієнтуються, у кристалах $\mathrm{Li_2Ge_7O_{15}}$

М.Д. Волнянський, М.П. Трубіцин, Ях'я А.Х. Обайдат

Дніпропетровський національний університет, кафедра фізики твердого тіла,
вул. Наукова 13, Дніпропетровськ 49050, Україна

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Раніше було показано, що у структурі кристалів гептагерманату літію $\mathrm{Li_2Ge_7O_{15}}$ домішкові іони хрому заміщують іони германію і створюють Cr^{3+}– Li^{+} парні центри. У роботі ЕПР і діелектричні спектри кристалів $\mathrm{Li_2Ge_7O_{15}{:}Cr^{3+}}$ досліджені у температурному діапазоні $300 \div 500$ K. Вперше термічно активована реорієнтація дипольних моментів Cr^{3+}– Li^{+} пар зареєстрована шляхом вимірювання поширення ЕПР ліній і діелектричної релаксації.

Ключові слова: *домішкові іони, електронний парамагнітний резонанс, діелектричні втрати і релаксація*

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