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Ising-type behaviour of critical properties in weak ferroelectric $Li_2Ge_7O_{15}$

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The dielectric constant ε and electron spin resonance spectra of Mn^{2+} ions have been studied in the range of the ferroelectric phase transition in $Li_2Ge_7O_{15}$ single crystals. Analysis of the experimental data permits one to estimate the critical exponents of dielectric susceptibility $\gamma \cong 1.25$, order parameter $\beta \cong 0.32$ and correlation length $\nu \cong 0.63$. The values of the critical exponents determined in a fairly broad temperature interval around T_c, are consistent with the theoretical predictions of the Ising model with a one-component non-polar ordering coordinate.

Key words: *weak ferroelectric, dielectric constant, electron spin resonance*

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1. Introduction

In $Li_2Ge_7O_{15}$ crystals, hereafter abbreviated as LGO, a second order transition from the paraelectric phase (space group D_{2h}^{14}) to the ferroelectric one (space group $C_{2\nu}^{5}$) occurs at temperature T_c=283.5 K [1,2]. The phonon mode, becoming soft on approaching T_c , was observed by the Raman scattering [3] and submillimeter spectroscopy [4]. As it was emphasized in [4], the soft mode is characterized by an extremely small effective charge and its contribution to the dielectric constant anomaly does not exceed 10% of the magnitude of ε peak at T_c. Dielectric investigations, carried out in the 21 MHz $\div$ 7 GHz frequency range [5], have revealed that another mode of a relaxational type becomes dominant near the transition point and gives the main contribution to ε anomaly. In accordance with X-Ray data [1], the structure of LGO crystals is formed by (GeO_4) and (GeO_6) polyhedral frameworks, whereas Li^+ ions are positioned in structural channels. The neutron diffraction study [6] allows one to associate the cooperative tilting motion of the (GeO_4) tetrahedrons with oscillator-type dynamics and shows that the motion of

Li^+ ions along the channels direction has a relaxational nature.

So, the physical properties of LGO crystals are characterized by a combination of the features usually attributed to displacive and order-disorder types of structural phase transitions. It seems that previous attempts to describe the temperature behaviour of the LGO dielectric constant [7] and the central peak intensity in hyper-Raman experiment [8] on the basis of the mean field approximation can be specified.

This paper reports the results of the dielectric constant ε and ESR measurements carried out in the range of the LGO phase transition.

2. Dielectric data

The studied LGO monocrystals were grown from the melt by the Chokhralsky method. The samples used in dielectric experiments were prepared as the plates of characteristic dimensions $10\times6\times1.6$ mm^3 with the polar axes $\overline{c}$ perpendicular to the largest plane. The dielectric measurements were performed at 1 kHz in the interval $273 \div 303$ K at cooling. The temperature was changed with the rate $\sim$ 0.2 K/min and controlled with the accuracy 0.02 K. The dielectric constant was measured with a precision higher than 10^{-3}.

The temperature behaviour ε(T) in the range of the transition point is represented in the insert to figure 1. The dielectric constant demonstrates a well-pronounced λ-shaped anomaly and reaches its maximal value $\sim$300 at $T^* =$ 283.92 K. The magnitude and sharpness of the ε peak manifests a much better quality of the investigated monocrystals in comparison with LGO samples studied in [7]. Since the dielectric constant below T_c may be affected by such artifacts as the domain walls motion, mobile imperfections effects etc., our attention is focused on the analysis of the ε(T) behaviour in a paraelectric phase.

At first we try to describe the dependence ε(T) within the framework of the Landau theory. The expression of the Curie-Weiss type

$$\varepsilon = \varepsilon_0 + \frac{C}{(T - T_c)}, \tag{1}$$

with three parameters – background ε_0, Curie-Weiss constant C and transition temperature T_c, is fitted by the least square method to the experimental data. The calculations are performed in the interval $T^* \leqslant T < 296$ K since above 296 K the dielectric constant varies very slowly and the real behaviour ε(T) is masked by experimental precision. The fitting procedure yields the following values:

$$\varepsilon_0 = 10.8;\ C = 3.5\ \mathrm{K};\ T_c = 283.93\ \mathrm{K}$$

with the relative mean square error $\sigma = 0.16$. An attempt to take into account the possible drift of the background dielectric constant and to represent it as $\varepsilon_0 = \varepsilon_0' + pT$ does not decrease the σ value.

Further, the experimental data are fitted by the exponential expression

$$\varepsilon = \varepsilon_0 + A(T - T_c)^{-\gamma}, \tag{2}$$

including additional parameter γ. The values calculated in the interval $T^* \leqslant T < 296$ K are as follows:

$$\varepsilon_0 = 11.0;\ A = 3.3\ \mathrm{K}^\gamma;\ \gamma = 1.25;\ T_c = 283.90\ \mathrm{K}$$

with σ=5.8×10^{-2}.

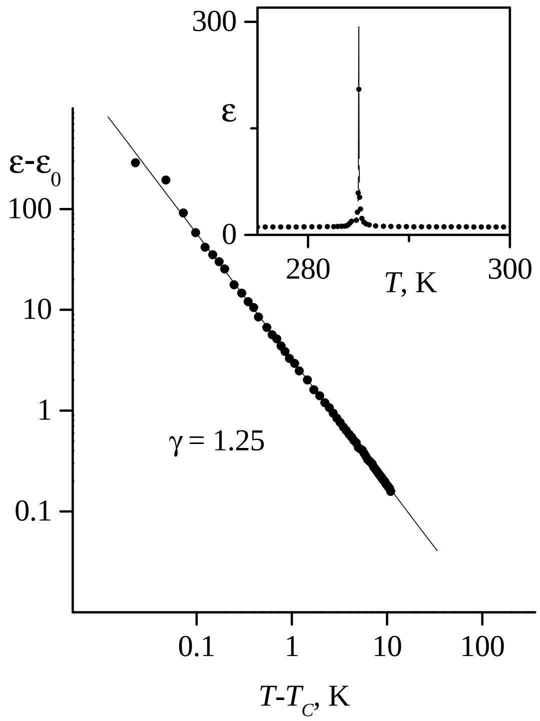

Figure 1. Dielectric constant $(\varepsilon - \varepsilon_0)$ versus $(T - T_c)$ in a log-log scale $(T > T_c)$. In the insert: dependence $\varepsilon(T)$ around T_c in an ordinary scale.

The obtained results clearly show that an assumption of a non-classical exponential behaviour (2) decreases the mean square error σ in approximately three times in comparison with the classical Curie-Weiss expression (1). Besides, the use of (2) gives a more reliable value of the transition point, whereas parameter T_c, obtained on the basis of the Curie-Weiss law (1), is higher than temperature T^* of the dielectric peak and hence slightly exceeds the real transition point.

So, it may be concluded that exponential expression (2) with a non-classical value of γ gives a better fit to the experimental data than the Landau theory. The temperature dependence of $(\varepsilon - \varepsilon_0)$ versus $(T - T_c)$, represented in figure 1 in a log-log scale, satisfactorily corresponds to a straight line with slope $\gamma \cong$1.25 in the interval considered.

It seems important to support the conclusion about the non-classical behaviour of the dielectric constant in LGO by alternative experimental techniques. In the next section we report some results of the electron spin resonance investigations of the ferroelectric phase transition in LGO.

3. Radiospectroscopic data

The ESR spectra were studied in LGO monocrystals doped with Mn^{2+} (0.06%; 0.2% wt) ions. The samples were cut as 3×3×4 mm^3 parallelepipeds with sides parallel to the main crystallographic planes. The spectra were measured on a conventional X-band spectrometer Radiopan SE/X 2547 equipped with a liquid nitrogen gas flow system. The localization of paramagnetic ions in the LGO lattice was determined on the basis of angular dependencies of Mn^{2+} spectra. The data reported earlier [9] give evidence that Mn^{2+} centers substitute Li^{+} ions in broad channels of the LGO structure with non-local compensation of the excess charge of the probe. It should be noted that the Mn^{2+} probe preserves the point symmetry of the host ion and, hence, does not drastically perturb the surroundings. So, one may hope, that ESR of manganese adequately reflects the critical properties of the perfect LGO structure.

In an ESR experiment, the information about statical and dynamical phenomena accompanying the structural phase transition can be obtained by measuring the ESR line position, width and shape. As it was shown in [10], on approaching T_c from above, the resonance lines of Mn^{2+} broaden and split into doublets in the ferroelectric phase.

The line splitting, observed below T_c, results from the correlated atomic distortions within a range of the paramagnetic probe. The local shift of the splitted resonance lines with temperature variations in the ferrophase is induced by the local order parameter and, consequently, reflects its magnitude. It may be shown that the distance ΔH between splitted spectral components is proportional to the local order parameter η_{loc}. So, measuring $\Delta H(T)$ allows one to investigate the temperature behaviour of η_{loc}. The dependence of ΔH versus $(T_c–T)$ is represented in figure 2 in a log-log scale. It is quite clear that the experimental behaviour in the interval $T_c - 10\mathrm{K} \leqslant T < T_c$ may be described by a straight line with the mean slope β ≅0.32, which appreciably differs from the classical value of the order parameter critical exponent 0.5. The dependence $\Delta H^2(T_c\text{-}T)$, represented in the insert to figure 2, demonstrates that the local order parameter behaviour significantly deviates from the Landau theory predictions in the low temperature vicinity of the transition point.

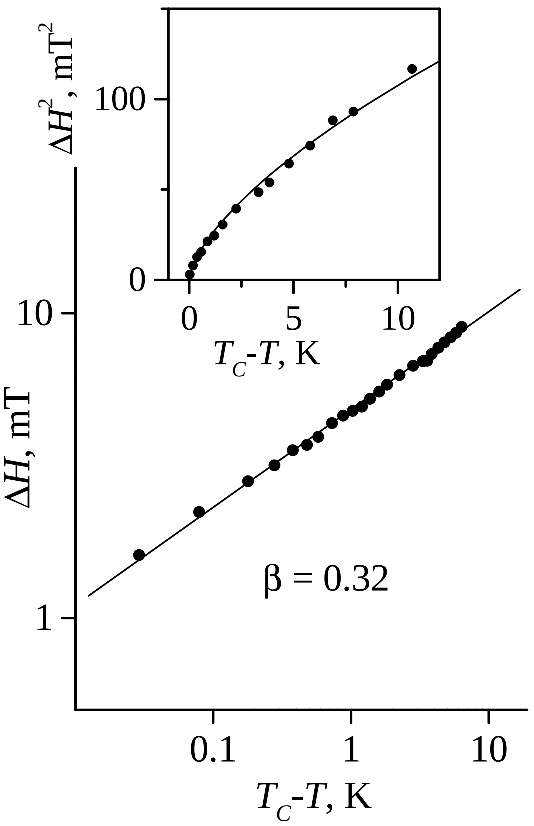

Figure 2. ESR line splitting ΔH versus $(T_c - T)$ in a log-log scale. In the insert: dependence $\Delta H^2(T_c - T)$ demonstrating deviation of the experimental behaviour from the Landau theory.

As it was mentioned above, the ESR lines anomalously broaden around T_c. The analysis of ESR spectra transformation via the phase transition shows that line width broadening is determined by inhomogeneous mechanisms and contributed by the local order parameter fluctuations $\delta\eta_{loc}$ [10]. Simulating the experimental line shape, we derived the critical contribution to the line width δH_{CR} and separated it from unessential background. The critical ESR line width dependence $\delta H_{CR}(T)$, measured on approaching T_c from above, is represented in a double logarithmic scale in figure 3. It can be seen that in the interval $T_c + 1K \leqslant T \leqslant T_c + 20K$ the experimental behaviour satisfactorily agrees with the exponential law $\delta H_{CR} \sim (T-T_c)^{-\nu}$. The mean slope of the $\delta H_{CR}(T-T_c)$ dependence in this interval permits one to estimate the critical index of the correlation length $\nu \cong 0.63$. In the narrow interval ~1K above T_c the dependence of the critical line width deviates from a straight line and tends to saturation (figure 3). This deviation may be interpreted as the result of partial suppression of local order parameter fluctuations by long-range dipole-dipole interactions.

4. Conclusions

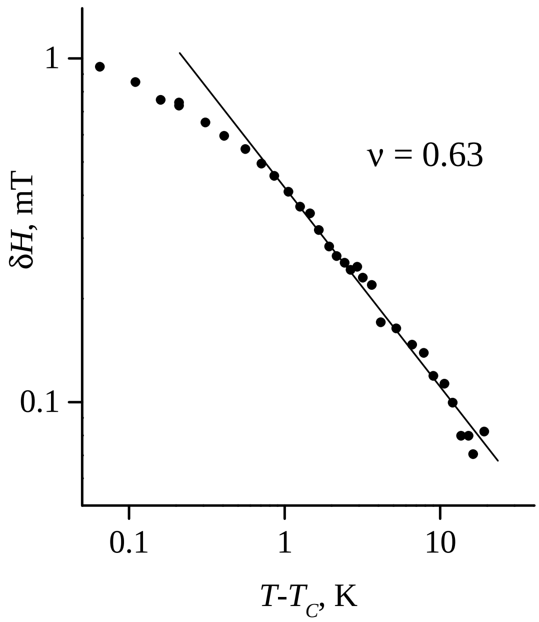

Figure 3. Temperature dependence of critical contribution to the ESR line width in a log-log scale.

Investigations of the dielectric constant and Mn^{2+} ESR spectra near the ferroelectric phase transition in LGO crystals allow one to determine the values of three critical indexes: the exponent of dielectric susceptibility $\gamma \cong 1.25$, order parameter $\beta \cong 0.32$ and correlation length $\nu \cong 0.63$. It is remarkable that the values of the critical exponents obtained in a fairly broad temperature range of T_c via studying the macroscopic and local properties are consistent with each other and correspond to the theoretical values given by a three-dimensional Ising model with a one-component non-polar ordering coordinate. Obviously, an extremely small soft mode effective charge predetermines the Ising-type behaviour of the LGO critical properties. Dipole-dipole interactions, mainly determining critical phenomena in classical uniaxial ferroelectrics, are no longer a decisive factor in LGO crystals. Consequently, order parameter fluctuations are well pronounced in a broad interval around T_c and lead to characteristic features peculiar to the order-disorder structural phase transition.

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Ізінгівська поведінка критичних властивостей слабкого сегнетоелектрика $Li_2Ge_7O_{15}$

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Діелектрична проникність ε та спектри ЕПР іонів Mn^{2+} досліджені в околі сегнетоелектричного фазового переходу у кристалах $Li_2Ge_7O_{15}$. Аналіз експериментальних даних дозволив оцінити критичні індекси діелектричної сприйнятливості $\gamma \simeq 1.25$, параметра порядку $\beta \simeq 0.32$ і кореляційної довжини $\nu \simeq 0.63$. Величини критичних індексів, обчислені у досить широкому інтервалі температур поблизу T_c, узгоджуються з теоретичними показниками моделі Ізинга для однокомпонентного неполярного параметра порядку .

Ключові слова: *слабкий сегнетоелектрик, діелектрична константа, електронний парамагнітний резонанс.*

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