Condensed Matter Physics, 1999, Vol. 2, No. 4(20), pp. 677–684

Ferroelectric phase transition in lead germanate $Pb_5Ge_3O_{11}$ studied by ESR of Gd^{3+} probe

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Received November 23, 1998

ESR spectra of Gd^{3+} probe have been studied in the range of ferroelectric phase transition T_{C}=451 K in lead germanate $Pb_5Ge_3O_{11}$. Measurements of ESR line position have shown that local order parameter behaves in accordance with the mean field theory approach in a broad (∼150 K) temperature interval below T_{C}. Anomalous line width broadening observed around T_{C} can be associated with a quasi-elastic central peak component of excitation spectrum, observed earlier using a light scattering experiment and attributed to static symmetry-breaking defects.

Key words: *ferroelectric phase transition, electron spin resonance*

PACS: *77.80.B*

1. Introduction

Lead germanate $Pb_5Ge_3O_{11}$ (PGO) has been the subject of intensive experimental and theoretical studies since the discovery of the structural phase transition from a high temperature paraelectric phase to a polar one at T_{C}=451 K [1, 2]. The crystal structure of PGO monocrystals, studied using neutron and X-ray diffraction [2–4], in non-polar phase corresponds to C^1_{3h} space group and on cooling below T_{C} spontaneous polarisation emerges along the **c**-axis of the trigonal C^1_3 structure. The unit cell of PGO contains three formulae units. The structural framework is constructed by alternative layers perpendicular to the polar axis and consisting of single $(GeO_4)^{4-}$ and paired $(Ge_2O_7)^{6-}$ germanium-oxygen tetrahedra connected by predominantly covalent Pb-O bonds [4]. From the microscopic point of view the structural distortions at the phase transition can be associated with tilt of $(GeO_4)^{4-}$ tetrahedra, twist of $(Ge_2O_7)^{6-}$ pyro- groups and displacements of Pb^{2+} ions [4]. Besides, the resulting dipolar moment emerges mainly due to $(Ge_2O_7)^{6-}$-groups distortion and Pb^{2+} ions displacements. Investigations of Raman [5, 6] and submillimetre spectra [7] reveal the softening of a low-frequency optic phonon and give evidence in favour of a displacive character of ferroelectric phase transition in PGO crystals. On approaching the transition point from ferrophase above ∼400 K, the soft phonon becomes overdamped, critical dynamics slow down and gain pronounced relaxation features peculiar to an order-disorder scheme of a structural phase transition. In addition to the overdamped soft mode, the central peak emerges in the excitation spectrum of lead germanate. Very refined light scattering experiment, performed in [6], makes it possible to resolve the line shape of the central peak and observe a weakly diverging, relatively broad (∼4 GHz) dynamic central component coexisting with a very narrow ($\leqslant$ 2 MHz) quasi-elastic central singularity. Although the microscopic reasons of the observed critical dynamics are not completely clear up to now, it has been assumed that the soft phonon reflects the oscillator type motion of Pb^{2+} ions whereas relaxation of $(GeO_4)^{4-}$ tetrahedra contributes to a dynamic central peak. The quasi-elastic central component is presumably originated from the frozen-in symmetry-breaking defects [6].

It is well known that magnetic resonance represents highly sensitive experimental techniques giving a unique information regarding static and dynamic phenomena accompanying structural phase transitions [8, 9]. ESR spectra of Gd^{3+} ions in lead germanate have been reported earlier [10–13]. It has been shown that Gd^{3+} ions predominantly occupy positions of trigonal point symmetry and substitute Pb^{2+} hosts in PGO lattice. Among the fifteen lead ions in the PGO unit cell, six structurally nonequivalent ions are positioned on the third order axis [4]. Theoretical analysis of the Gd^{3+} spectra, performed in [14] based on the point-charge approximation and superposition model, allows us to assume that gadolinium most probably substitutes Pb(4) ions in accordance with the earlier conclusions [10]. Since the paramagnetic probe preserves the local symmetry of the host, it may be suggested that the excess charge introduced by the probe is compensated non-locally.

The attention in the papers [10–13] was focused mainly on the details of Gd^{3+} centers localization and possible mechanisms of the paramagnetic probe charge compensation. It seems that additional valuable information can be derived by applying the ESR techniques to the study of static and dynamic properties of PGO in the range of ferroelectric phase transition.

2. Theoretical background

ESR spectra in the range of structural phase transition can be described by usual spin- Hamiltonian (SH) formalism based on the perturbation theory

$$H_{\mathrm{FP}} = H_{\mathrm{PP}} + H'. \tag{1}$$

Here H_{PP} represents hexagonal SH appropriate to C_{3h} local symmetry of the probe in paraelectric phase; H'-“perturbing” SH which contains trigonal spin operators and describes lowering of the Gd^{3+} local symmetry at the phase transition [15]

$$H' = b_4^3 O_4^3 + c_4^3 \Omega_4^3. \tag{2}$$

Parameters of "perturbing" SH H' are the functions of the correlated atomic distortions in the range of paramagnetic probe. Consequently near T_C the resonance fields can be expanded in powers of the time dependent local order parameter $\eta(t) = \langle\eta\rangle + \delta\eta(t)$

$$\begin{aligned} B_R(t) &= B_0 + a\eta + \frac{1}{2}b\eta^2 + ... \\ &= B_0 + a\langle\eta\rangle + \frac{1}{2}b\langle\eta^2\rangle + \left[a\delta\eta + \frac{1}{2}b(\eta^2 - \langle\eta^2\rangle)\right]. \end{aligned} \tag{3}$$

Here B_0 represents the line position above T_C. Expansion coefficients a, b are determined by secular and non-secular matrix elements of SH H' correspondingly. Hence parameters a, b depend on the probe site and magnetic field direction with respect to the crystallographic axes. It can be shown that if the local symmetry, accounting for the external magnetic field effect, contains elements destroyed at the phase transition, all odd terms in expansion (3) should vanish. As it has been shown in [10, 11], on cooling below T_C the local symmetry of Gd^{3+} probe reduces from hexagonal C_{3h} to trigonal C_3 point group, i.e. the mirror plane perpendicular to polar axis vanishes in ferroelectric phase. It means, that applying external magnetic field **B** along or perpendicular to **c**-axis, one can provide quadratic coupling of resonance fields with the local order parameter (a=0). For general orientation of **B**, the linear term in expansion (3) becomes non-zero and both terms - linear and quadratic should contribute to resonance fields.

3. Experimental results and discussion

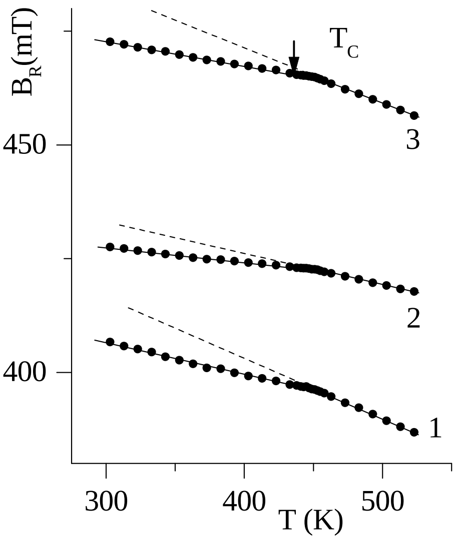

Figure 1. Temperature dependencies of line positions $M_S = -5/2\beta - 7/2$ (1), $-1/2\beta - 3/2$ (2), $-3/2\beta - 5/2$ (3). $\mathbf{B} \parallel \mathbf{c}$.

PGO monocrystals were grown from the melts by Czhokhralskii method with addition of Gd_2O_3 (0.01 wt. percent). The samples studied were cut off as parallelepipeds of 3x3x3 mm^3 typical dimensions with edges parallel to crystallographic axes. ESR spectra were registered by conventional X-band spectrometer. The temperature of the samples was regulated by nitrogen gas flow cryostat.

ESR spectrum of Gd^{3+} in ground state $(4f^7, {}^8S_{7/2})$, consisting of seven fine structure components $\Delta M_S = \pm 1$, was registered. In paraelectric phase the angular variations of spectra reveal C_{3h} local symmetry of active probe site with a third order axis parallel to a unique polar axis **c**. On cooling below T_C for general orientations of external magnetic field **B** the outer fine structure lines $M_S = \pm 1/2\beta \pm 3/2; \pm 3/2\beta \pm 5/2; \pm 5/2\beta \pm 7/2$ split into doublets in accordance with the reducing of the local symmetry to C_3 group [16] and the emerging of 180^0 domains with antiparallel direction of spontaneous polarization. The symmetry of ESR spectra and SH parameters undoubtedly show that Gd^{3+} centers studied in this work have got the same nature as the ones investigated earlier in [10, 11].

Temperature dependencies of positions $B_R(T)$ of three high field ESR lines $M_S = -1/2\beta - 3/2; -3/2\beta - 5/2; -5/2\beta - 7/2$, measured at orientation $\mathbf{B} \parallel \mathbf{c}$, are plotted in figure 1. It can be seen that in the paraelectric phase, resonance lines linearly shift to high field side due to the lattice contraction effect. Below T_C, line positions change their behaviour. Experimental points deviate from dashed lines extrapolating to ferroelectric phase the thermal drift of line position B_0 above T_C. In accordance with simple theoretical description briefly given above, the static part of expansion (3) determines the shift of the line position induced by the local order parameter. For main orientation $\mathbf{B} \parallel \mathbf{c}$ the linear term in (3) is forbidden by symmetry. So, the experimental data, represented in figure 1, can be described by

$$B_R = B_0 + \frac{1}{2} b \langle \eta \rangle^2, \tag{4}$$

with accounting of the B_0 thermal drift above T_C and ignoring negligible fluctuation contributions, i.e. assuming $\langle \eta^2 \rangle = \langle \eta \rangle^2$. It is clear, that deviation of experimental points from dashed lines (figure 1) results from the contribution of the local order parameter squared with negative parameter $b < 0$ (4). From figure 1 it can be seen that experimental dependencies can be satisfactorily described by the straight lines $[B_0(T) - B_R(T)] \sim \langle \eta \rangle^2 \sim (T_\mathrm{C} - T)$ in accordance with the mean field theory approach.

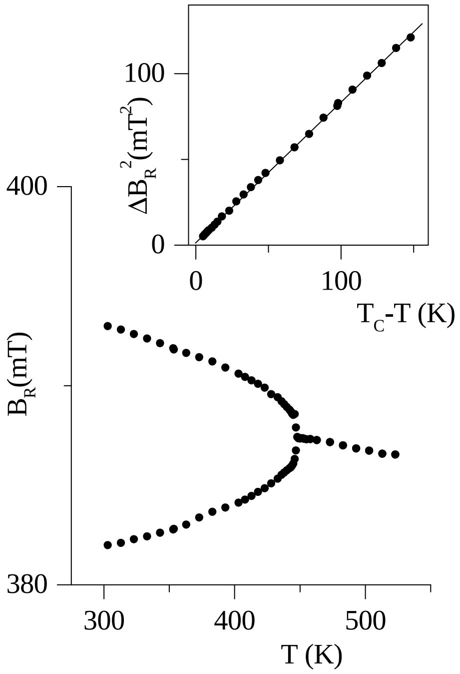

Figure 2. Line position of $M_S = -5/2\beta 7/2$ at $\angle \mathbf{B}, \mathbf{c} = \mathbf{44^0}, \mathbf{B} \perp \mathbf{b}$ in the range of T_C=451 K. In the insert: line splitting squared ΔB^2 vs $(T_\mathrm{C} - T)$.

Naturally the line position should be more sensitive to a local order parameter magnitude for general orientations of the external magnetic field, allowing non-zero linear term in expansion (3). The experimental dependency of $M_S = -5/2\beta - 7/2$ line position at $\angle \mathbf{B}, \mathbf{c} = \mathbf{44^0}, \mathbf{B} \perp \mathbf{b}$ is presented in figure 2. Single ESR line slightly shifts to high fields and below T_C splits into two components, resulting from nonzero value of the local order parameter $\pm\langle \eta \rangle$. In accordance with (3), positions of the splitted components are given by

$$B_{R1,R2} = B_0 \pm a \langle \eta \rangle + \frac{1}{2} b \langle \eta \rangle^2. \tag{5}$$

From this expression it follows that the distance between components of doublet is proportional to the first order of local order parameter

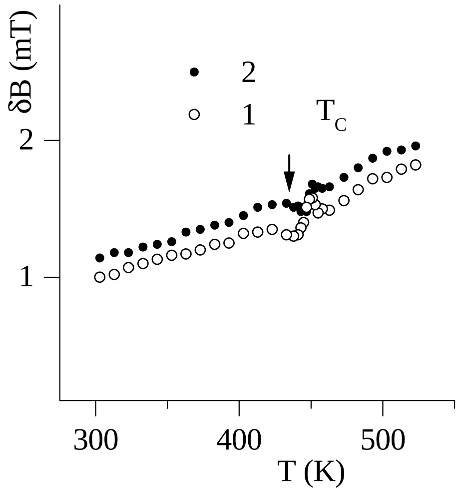

Figure 3. Temperature dependencies of line width $M_S = -3/2\beta - 5/2$ (1), $-5/2\beta - 7/2$ (2). $\mathbf{B} \parallel \mathbf{c}$.

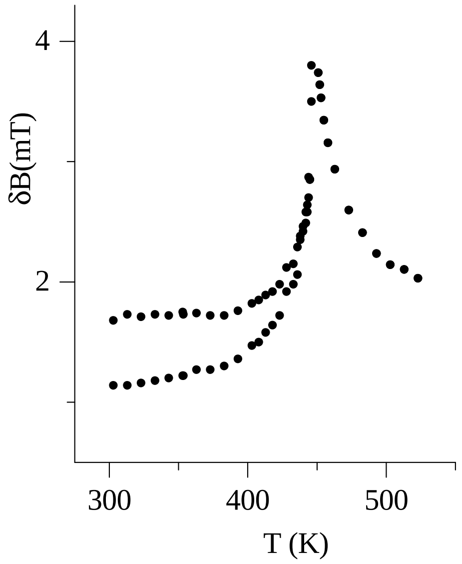

Figure 4. Anomalous line width broadening. $M_S = -5/2\beta - 7/2$, $\angle\mathbf{B},\mathbf{c} = \mathbf{44^0}, \mathbf{B}\perp\mathbf{b}$.

$$\Delta B = B_{R1} - B_{R2} = 2a\langle\eta\rangle.$$

In the vicinity of transition point 448÷451 K the line splitting is masked by anomalous line width broadening and line position determination demands a more refine analysis of the spectral contour. Excluding this temperature interval, least square fitting of equation (5) to experimental data gives the value of transition point of 450.5 K. Fitting the line splitting ΔB vs $(T_C - T)$ in a double logarithmic scale gives for T_C the value of 451.4 K. Hence T_C=451 K can be accepted as experimentally measured transition point with ± 0.5 K uncertainty. Squared line splitting ΔB^2 vs $(T_C - T)$ is plotted in the insert to figure 2. It is quite clear that experimental points well correspond to the straight line up to $(T_C - T) \sim 150$ K, confirming the classic behaviour of the local order parameter $\langle\eta\rangle \sim (T_C - T)^{1/2}$.

Besides the line positions, width of ESR lines demonstrates pronounced anomaly in the range of T_C. Temperature dependencies of peak to peak line width for $M_S = -3/2\beta - 5/2; -5/2\beta - 7/2$ at $\mathbf{B} \parallel \mathbf{c}$ are presented in figure 3. Weak but distinctly visible anomalies of line width can be seen around T_C. These anomalies result from the local order parameter fluctuations and can be described by the time dependent part of resonance fields expansion (3). Since for the main orientation $\mathbf{B} \parallel \mathbf{c}$, linear term in (3) is forbidden by symmetry, detected anomalies can be attributed to the quadratic term originated from two-phonon relaxation processes. Weakness of line width increasing for $\mathbf{B} \parallel \mathbf{c}$ does not make it possible to analyze the anomalies quantitatively.

Temperature dependence of $M_S = -5/2\beta - 7/2$ line width, measured at general orientation ($\angle\mathbf{B},\mathbf{c} = \mathbf{44^0}, \mathbf{B}\perp\mathbf{b}$), is depicted in the figure 4. A well pronounced λ- shaped anomaly has been observed around T_C. Line width δB increases from ~ 2.0 mT at 523 K to ~ 3.8 mT closely to transition point. Anomalous line width broadening is accompanied by changes of line shape and results exceptionally from increasing of the gaussian component [17]. It can be seen that in ferroelectric phase both splitted components have got different widths on cooling away from T_C. As it has been shown above for general orientation chosen, coupling between resonance fields and local order parameter (3) is dominated by a linear term. Critical contribution to the line width can be expressed through the resonance line second moment

$$\delta B_{CR}^2 = 4(\langle B_R^2\rangle - \langle B_R\rangle^2) \sim (a \pm b\langle\eta\rangle)^2 \sum\nolimits_q \langle \delta\eta_q^2\rangle. \tag{6}$$

Since ESR measures the local properties of the probe, the sum in (6) gets over fluctuations with all wave vectors within Brillouin zone. Hence, pronounced line width broadening reflects the critical divergence of the order parameter susceptibility, connected with mean square fluctuations by fluctuation-dissipation theorem. As it can be seen from the factor $(a \pm b\langle\eta\rangle)^2$ before the sum in (6), different widths of two splitted components below T_{C} may arise from the second order term contribution. Inhomogeneous gaussian character of line width broadening gives evidence that order parameter fluctuations, contributing to line width anomalies, are slow in comparison with the frequency analogue of the background non-critical ESR line width $\sim$ 30 MHz.

4. Conclusions

Lead germanate undergoes ferroelectric phase transition with the emerging of spontaneous polarization along the unique trigonal axis. Hence it belongs to the universality class of the systems with one-component polar order parameter where long-range dipole-dipole interactions predetermine applicability of mean field theory around transition point [18]. In agreement with this assertion, ESR line position data of Gd^{3+} probe demonstrate classic behaviour of the local order parameter in a broad temperature interval of ferroelectric phase.

Anomalous line width broadening, observed for general orientations of external magnetic field around T_{C}, is determined by increasing of inhomogeneous gaussian component. It may be concluded, that critical line width is contributed by quasi-static order parameter fluctuations with frequencies less than $\sim$ 30 MHz. Detailed measurements of the Gd^{3+} line width anisotropy, performed recently in [19], have shown that the main contribution to line width involve triclinic spin operators $(b_2^1 O_2^1 + c_2^1 \Omega_2^1)$ by contrast to trigonal symmetry of the "perturbing" SH H' (2), which determines line splitting in ferroelectric phase. Authors of [19] have assumed that triclinic anisotropy of the critical line width results from the non-local charge compensators statistically positioned relative to the paramagnetic ion location. Perhaps that anisotropy of line width is not necessarily to connect with non-local charge compensators but it is quite sufficient to consider a possible influence of symmetry-breaking defects of any sort. It seems that the observed features of ESR line width broadening may be associated with a very narrow elastic central peak component, detected in light scattering experiment [6] and presumably originated from frozen-in symmetry-breaking defects. Obviously the range of influence of such defects becomes infinitely large as the correlation length diverges on approaching T_{C} and anisotropy of ESR critical line width could be reduced.

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EPR spectrum broadening in $Pb_5Ge_3O_{11}$ near structural transition. // Solid State Phys. (Russia), 1998, vol. 40, No. 2, p. 321–326 (in Russian).

Дослідження методом ЕПР сегнетоелектричного фазового переходу у кристалах германату свинцю $Pb_5Ge_3O_{11}$:Gd^{3+}

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Отримано 23 листопада 1998 р.

ЕПР спектри іонів Gd^{3+} вивчалися в інтервалі сегнетоелектричного фазового переходу T_c=451 К кристалів германату свинцю $Pb_5Ge_3O_{11}$. На підставі вимірювання температурних залежностей положення ЕПР ліній показано, що поведінка локального параметра порядку в досить широкому інтервалі ($\sim$ 150 К) сегнетоелектричної фази погоджується з теорією середнього молекулярного поля. Аномальне розширення резонансних ліній, що спостерігається навколо T_c, може бути зіставлене з вузьким квазі-пружним центральним піком у спектрах комбінаційного розсіяння світла і пов'язане зі статичними дефектами кристалічної гратки.

Ключові слова: *сегнетоелектричний фазовий перехід, електронний парамагнітний резонанс*

PACS: *77.80.B*