

Pseudo-Stark splitting induced by a phase transition in the optical spectra of ferroelectrics with dipole impurity centers

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A splitting of R lines has been observed in the course of the $D_{2h} \rightarrow C_{2v}$ phase transition in $\text{Li}_2\text{Ge}_7\text{O}_{15}:\text{Cr}^{3+}$ crystals. This splitting indicates that the ensemble of Cr^{3+} centers of the paraelectric phase splits into two physically nonequivalent ensembles in the course of the transition to the ferroelectric phase. This effect stems from the triclinic local symmetry of the Cr^{3+} centers, which have a dipole moment. The splitting of the R lines is a "pseudo-Stark" splitting in the odd internal crystal field induced in the ferroelectric phase by a polar order parameter.

Studying the effects of structural phase transitions in the optical spectra of impurity ions serving as probes is an important method in spectroscopic research on the properties of phase transitions in crystals.¹ In this letter we are reporting the first observation of a specific splitting of spectral lines of impurity centers in the course of a ferroelectric phase transition. This splitting occurs because dipole centers with different orientations in the lattice, which are physically equivalent in the centrally symmetric paraelectric phase, become physically nonequivalent upon the transition to the polar ferroelectric phase.

The experiments were carried out on single crystals of lithium heptagermanate, $\text{Li}_2\text{Ge}_7\text{O}_{15}$ (LGO), activated with $\text{Cr}^{3+}(3d^3)$ ions. In the paraelectric phase ($T > T_c = 10^\circ\text{C}$), LGO crystals belong to the centrally symmetric orthorhombic class D_{2h} , while in the ferroelectric phase ($T < 10^\circ\text{C}$) they belong to the polar orthorhombic class C_{2v} (Refs. 2 and 3). In LGO: Cr^{3+} activated crystals, the Cr^{3+} ions replace Ge^{4+} ions in an octahedral neighborhood of six oxygen ions (GeO_6). Two pairs of R lines are observed in the optical spectra of the ferroelectric phase of LGO: Cr^{3+} at low temperatures ($T < 190\text{ K}$): ${}^4A_2\text{-}{}^2E$ (at $T = 2\text{ K}$, the R_1 and R_2 lines are at $14\,360$ and $14\,423\text{ cm}^{-1}$, while R'_1 and R'_2 are at $14\,375$ and $14\,430\text{ cm}^{-1}$; see the inset in Fig. 1). These pairs of lines belong to Cr^{3+} centers of two types (R and R'), which differ slightly in the positions of the lower (\bar{E}) and upper ($2\bar{A}$) excited sublevels¹⁾ of the 2E doublet.⁴ The (nonuniform) width of the lines R_1 and R'_1 is 1.5 cm^{-1} at 2 K . The line R_2 is considerably broader (6 cm^{-1}), because of a pronounced homogeneous broadening resulting from the fast $2\bar{A} \rightarrow \bar{E}$ one-phonon relaxation.

We have carried out a detailed study of the behavior of the R_1 and R'_1 luminescence lines of LGO: Cr^{3+} over a broad temperature range ($2\text{--}310\text{ K}$), which includes the point of the phase transition. We measured the temperature (T) dependence of Δ , the frequency distance between the narrower lines, R_1 and R'_1 (Fig. 1). The dots (or small filled circles) correspond to measurements of $\Delta(T)$ in the low-temperature re-

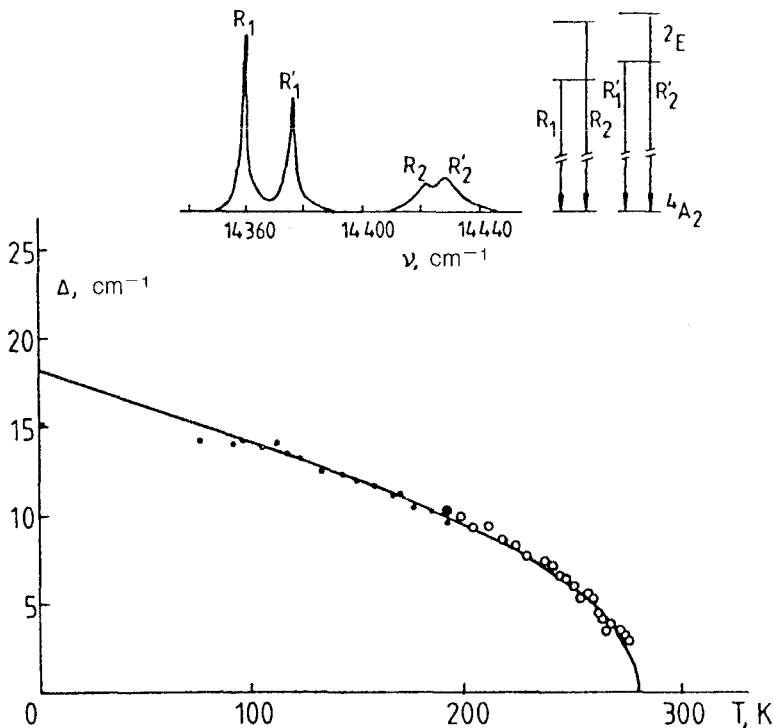


FIG. 1. Temperature dependence of the distance between the lines R_1 and R'_1 in the luminescence spectrum of LGO:Cr³⁺. The points are experimental, while the solid line shows a calculation of $\Delta(T) = 1.05 \times (279 - T)^{1/2}$. The inset shows the luminescence spectrum of LGO:Cr³⁺ at $T = 77$ K, along with a scheme of the transitions at the R and R' centers.

gion ($T < 190$ K), in which R_1 and R'_1 are spectrally resolved. The open circles show the results of measurements at $T > 190$ K, where the R_1 and R'_1 lines overlap because of their thermal broadening, and where $\Delta(T)$ was found by modeling the resultant unresolved $R_1 + R'_1$ line as the sum of two Lorentzian lines R_1 and R'_1 , with a relative shift of Δ . The homogeneous thermal broadening of the lines was taken into account.

It can be seen from Fig. 1 that as the ferroelectric phase of LGO:Cr³⁺ is heated from liquid-helium temperature, the frequency interval (Δ) between R_1 and R'_1 decreases monotonically. As the point of the phase transition, T_c , is approached, $\Delta(T)$ rapidly drops to zero. The lines R_1 and R'_1 merge at the point T_c , and above T_c the R_1 line alone exists in the paraelectric phase of LGO:Cr³⁺. It follows directly that the single type of Cr³⁺ center in the paraelectric phase of LGO splits into two physically nonequivalent types of centers in the course of the phase transition to the ferroelectric phase ($T < T_c$). The idea that the centers of the two types (R and R') in the ferroelectric phase of LGO:Cr³⁺ have a common origin also agrees with the close spacing of the spectral lines in the $R_1 - R'_1$ and $R_2 - R'_2$ pairs. It furthermore agrees with the approximate equality of the radiative times of the R and R' centers (5 and 6.5 ms,

respectively⁴). A similar transformation of Cr^{3+} centers of one type into centers of two types in the course of a phase transition from the paraelectric phase to the ferroelectric phase has been seen⁵ in the ESR spectra of $\text{LGO}:\text{Cr}^{3+}$.

In order to reach an understanding of the nature of the observed transformation of the centers in $\text{LGO}:\text{Cr}^{3+}$ in the course of the phase transition, it is extremely important to look at the results of research on the symmetry properties of the centers which has been carried out by studying the effect of an external electric field on the R_1 and R'_1 lines in the ferroelectric phase of $\text{LGO}:\text{Cr}^{3+}$ (Refs. 6 and 7). In an external field E directed along the orthorhombic axes a, b, c , one observes a symmetric "pseudo-Stark"⁸ splitting of the lines which is linear in $|E|$. This splitting occurs because of a difference between the linear Stark frequency shifts $\Delta\nu = (\mathbf{d}\cdot\mathbf{E})$ of the transitions of dipole centers (without an inversion center), which differ only in their orientation in the lattice and which therefore have equal projections of the "effective" dipole moment \mathbf{d} onto the external field \mathbf{E} ($\mathbf{d} = \mathbf{d}^* - \mathbf{d}_0$, where \mathbf{d}^* and \mathbf{d}_0 are the constant dipole moments in the two electron states of the center between which the electron transition occurs). It follows^{6,7} from the experimental pattern of the pseudo-Stark splitting of R_1 and R'_1 that the direction of \mathbf{d} for the R_1 and R'_1 centers in the LGO lattice is approximately along the a axis. [We have $d_a = 0.35 \times 10^{-5} \text{ cm}^{-1}/(\text{V}/\text{cm})$ for R_1 and $d_a = 0.19 \times 10^{-5} \text{ cm}^{-1}/(\text{V}/\text{cm})$ for R'_1 ; the projection of \mathbf{d} onto the b axis is an order of magnitude smaller; the projection into the ferroelectric c axis is not seen at all

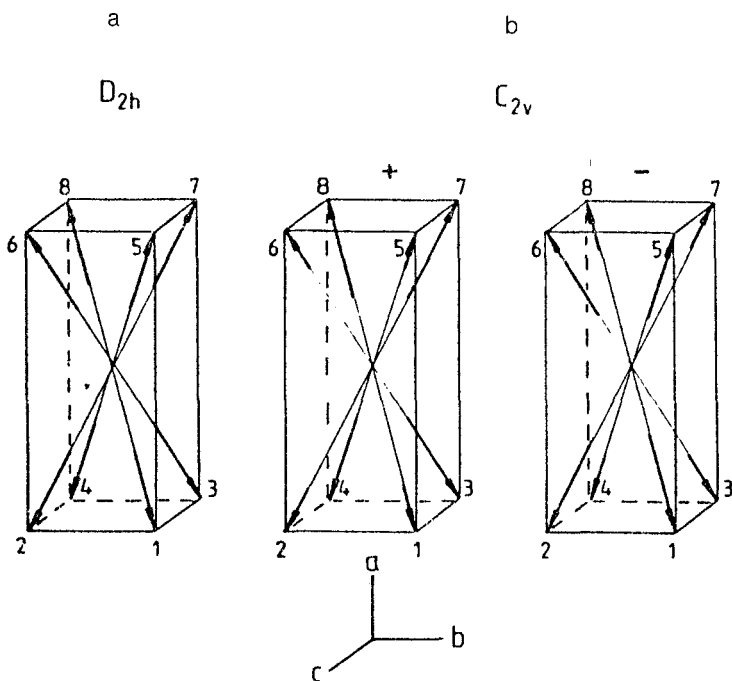


FIG. 2. Orientation of the dipole moments of the C_1 centers (a) in the lattice of the paraelectric phase, D_{2h} , and (b) in the domains of the ferroelectric phase, C_{2v} .

experimentally.] This orientation of \mathbf{d} in the lattice is unambiguous evidence^{6,7} of a triclinic inversionless symmetry of the R and R' centers of LGO:Cr³⁺ (point group C_1). The conclusion that the centers in LGO:Cr³⁺ have a C_1 symmetry is also based on a study of ESR spectra.⁵

Let us analyze the properties of the ensemble of C_1 centers in the orthorhombic lattice of LGO, both in its paraelectric phase (D_{2h}) and after the phase transition to the ferroelectric phase (C_{2v}). In the D_{2h} paraelectric phase, the number of physically equivalent sites of C_1 Cr³⁺ centers which differ in orientation (this is an orientational degeneracy) is $G/g = 8$, where $G = 8$ and $g = 1$ are the orders of the symmetry group of the crystal (D_{2h}) and the symmetry group of the center (C_1), respectively. Figure 2a is a schematic diagram of the orientations of the dipole moments \mathbf{d} of these eight sites of the centers. These results were found by applying the operations of symmetry group D_{2h} .

In the C_{2v} ferroelectric phase ($G = 4$), the number (G/g) of physically equivalent sites of centers with the symmetry C_1 ($g = 1$) is 4. In the course of the $D_{2h} \rightarrow C_{2v}$ phase transition, the ensemble of eight sites of the centers should break up into two physically nonequivalent ensembles, each containing four sites differing in orientation. From the symmetry standpoint, this result explains the appearance of Cr³⁺ centers of two types, R and R' , in LGO:Cr³⁺ at $T < T_c$ from the center of a single type observed in the paraelectric phase. The sites corresponding to the R and R' centers in the ferroelectric phase are shown schematically in Fig. 2b (by means of \mathbf{d} arrows of a different length). Corresponding to the two ensembles, R and R' , in one ferroelectric domain (and to R' and R , respectively, in the other) are the sites (1,2,5,6) and (3,4,7,8) which differ in the sign of the projection of \mathbf{d} onto the polar ferroelectric c axis of the domain (the C_2 axis of the C_{2v} group of the paraelectric phase).

We explain the observed doublet splitting of the R_1 line at $T < T_c$ (Fig. 1) in the following way. For the R and R' centers, for which the projections of d_c onto the polar c axis of a domain differ in sign, the linear Stark shifts of the electron levels and of the frequencies of the optical transitions differ in sign. This Stark shift is caused by the odd crystal electric field E_{loc} , which is directed along the c axis. This field is induced at the position of the Cr³⁺ ion by the polar order parameter $\vec{\eta}$ ($E_{loc} \propto \vec{\eta}$). The observed splitting of the R_1 line in the ferroelectric phase (Fig. 1) may thus be thought of as a sort of pseudo-Stark splitting of the line in the internal electric field induced in the ferroelectric phase by the order parameter $\vec{\eta}$.

The measured temperature dependence of the splitting, $\Delta(T)$, can be described well over a broad temperature range (Fig. 1) by the square-root law $\Delta(T) = (T_c - T)^{1/2} \cdot (1.05 \text{ cm}^{-1}/K^{1/2})$, where $T_c = 6^\circ \text{C}$. A $(T_c - T)^{1/2}$ dependence is characteristic of the temperature dependence of the order parameter of a continuous second-order phase transition, which the phase transition in LGO is.^{2,3} The vector order parameter in LGO corresponds to a slightly polar optical mode $\vec{\eta}$ at the center of the Brillouin zone.⁹ The pseudo-Stark splitting Δ is linear in the internal field and arises from the oppositely directed shifts of the R lines of the Cr³⁺ centers with \mathbf{d} projections onto the ferroelectric c axis which differ in sign. It can be assumed that this splitting satisfies $\Delta \propto (d_c E_{loc}) \propto \eta \propto (T_c - T)^{1/2}$. The shape of the experimental $\Delta(T)$ dependence can thus be explained in a natural way in terms of a pseudo-Stark splitting

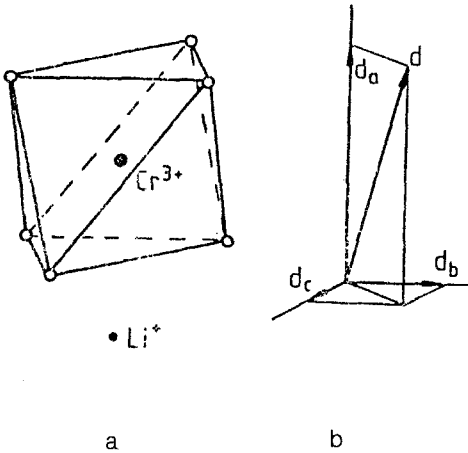


FIG. 3. Model of a Cr^{3+} center⁵ and schematic diagram of its dipole moment.

in the internal field. It follows from an experimental estimate⁷ of d_c [$< 10^{-6}$ cm⁻¹ / (V/cm)] that the maximum observed splitting $\Delta \approx 15$ cm⁻¹ corresponds to odd internal fields $\sim 10^7$ V/cm.

We thus see that the splitting of the R lines of LGO: Cr^{3+} in the course of the phase transition is influenced in a decisive way by the circumstance that the dipole moment of the Cr^{3+} centers has a component along the ferroelectric c axis. Such a projection arises only if the centers have a complex structure. In the regular LGO lattice (D_{2h}), the site of the Ge^{4+} ion replaced by the Cr^{3+} ion in the octahedral neighborhood (Fig. 3) has a monoclinic point symmetry (group C_2) with a twofold axis $C_2 \parallel b$. According to the symmetry conditions,¹⁰ the dipole moment at such a center is parallel to $C_2 \parallel b$. The experiments of Refs. 6 and 7, however, indicate a lower, triclinic C symmetry of the center, with d directed nearly parallel to a . According to the model proposed for the center,⁵ the center in LGO: Cr^{3+} contains not only a Cr^{3+} ion but also a nonstoichiometric Li^+ ion (Fig. 3). This Li^+ ion, which locally cancels the excess charge of Cr^{3+} (Ge^{4+}), is a neighboring octahedral void, displaced along the a direction with respect to the Cr^{3+} ion. According to the experiments of Refs. 5–7, the point symmetry of such a center is triclinic, C_1 . It is easy to show that the Coulomb field of Li^+ induces in the Cr^{3+} ion (a site with the symmetry C_2) not only the “original” moment parallel to $C_2 \parallel b$ but also two other components of \mathbf{d} , which lie in the plane perpendicular to C_2 (Fig. 3). The component d_a (on the $\text{Cr}^{3+} - \text{Li}^+$ line) is obviously the largest, and the component perpendicular to it (d_c) is small (this situation, $d_a \gg d_c$, is seen in the pseudo-Stark splitting in an external field^{6,7}). Consequently, it is only by virtue of the charge-canceling Li^+ ion that the centers in LGO: Cr^{3+} have a projection of \mathbf{d} onto the ferroelectric axis (although this projection is very small). The existence of this projection is a fundamental requirement for the very existence of a pseudo-Stark splitting of the R lines in the internal field in the course of the LGO: Cr^{3+} phase transition. This splitting reflects the splitting of an ensemble of centers which are of a single type at $T > T_c$ into two ensembles at $T < T_c$.

The observed physical nature of the splitting of the spectral lines in the course of the ferroelectric phase transition in LGO:Cr^{3+} , associated with the lifting of the orientational degeneracy of the centers in the external field in the ferroelectric phase, is fundamentally different from that of the splitting of the Cr^{3+} lines in the course of the structural phase transition in SrTiO_3 , which was described in Ref. 11. In the latter case, the splitting of the R lines results from a splitting of orbitally degenerate levels of an individual ion as the symmetry of the local crystal field lowers in the course of the phase transition.

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¹⁾We are using the notation for the 2E sublevels of Cr^{3+} in ruby.

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