interaction of charge dislocations with luminescence centers in ZnS crystals

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The stationary luminescence produced when ZnS crystals are deformed (deformation luminescence—DL) is investigated. It is proved that this phenomenon is of dislocation origin and a mechanism is proposed for it. The effective interaction radius of charged dislocations with purposely produced electron centers located 0.7–0.8 eV from the bottom of the conduction band is found by experiment to be $R_e \sim 10^{-6}$ cm.

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1. INTRODUCTION

It was previously established[1-3] that plastic deformation of II–VI crystals, depending on the experimental conditions, is accompanied by both pulsed and stationary luminescence. The pulsed deformation emission investigated by us in detail before[1,2] is electroluminescence produced on the crystal surface when electric charge is accumulated on the faces of the deformed sample as a result of the motion of charged dislocations.

We study in this paper the spectral and temperature characteristics of the stationary deformation luminescence (DL) of Zn crystals. A parallel investigation of deformation emission, photoluminescence, and electric characteristics of the deformed sample have made it possible to establish that the DL is the result of excitation of luminescence centers by moving charged dislocations. A DL mechanism is proposed and consists of tunneling of the electrons from the luminescence centers into the conduction band in the strong electric field of a moving charged dislocation, followed by radiative recombination of these electrons on the ionized luminescence centers.

2. SAMPLES. CHARACTERISTICS OF DISLOCATIONS

The single crystals were grown by the Bridgman method in an argon atmosphere at a pressure 150 atm. We investigated crystal doped with Mn and Cu and additionally coactivated with Al_2S_3 to stablize the 6*H* structure.[1)] The specific thermal resistivity ρ of the crystals was $\rho \sim 10^{10} - 10^{11}\ \Omega\cdot\text{cm}$. Samples measuring 2 × 2 × 4 and 3 × 3 × 6 mm and having a 6*H* structure were cut in such a way that their basal plane made an angle 45° with the deforming stress. The samples were plastically deformed at a constant rate in a specially constructed setup. The deformation rate $\dot{h}$ could be varied between 1 and 1000 μm/min, and the temperature was maintained constant within 0.5° in the interval 300 – 500 K.

The luminescence produced by the plastic deformation was registered with a low-noise high-sensitivity photomultiplier, FÉU-79 or FÉU-106, using thermoelectric microrefrigerators to cool the photocathode and bulb of the photomultiplier. This decreased the dark noise level of the photomultiplier and made it possible to register light fluxes of 30–50 photons per second. For the spectral investigations we used the large-aperture MDR-3 monochromator. The photoluminescence was excited with a DKSSh-120 xenon lamp through a DMR-4 monochromator.

To determine the dislocation charge, indium contacts were produced on the $(10\bar{1}1)$ face of the crystal by ultrasonic soldering. The signal from the contacts was applied to the input resistance of an electrometric amplifier, and the sample resistance R_s in all the investigations was larger than the electrometer input resistance: $R_s \gg R_{\text{in}}$. The procedure for measuring the nonlinear charge density q of the dislocation is described in detail in Ref. 2.

The dislocation structure of II-VI crystals, particularly ZnS, can be quite varied.[4] The plastic deformation can be the result of motion of both perfect (30°, 60°, edge, screw) and partial dislocations. An important feature of ZnS single crystals is the presence of structural microtwin-sphalerite and 6*H* structure—sphalerite phase transitions produced in plastic deformation.[5,6] The investigations reported in Refs. 5 and 6 have shown that partial dislocations move in the basal plane (0001) under plastic deformation.

The dislocations in ZnS and ZnSe crystals are charged, and experimental observation of the dislocation charge was reported earlier.[7,8] Detailed investigation of the linear charge density of the dislocations and of its dependence on the sample temperature and on the rate of the plastic deformation are reported in Refs. 2, 9, and 10. The linear charge density of the dislocations in pure ZnS crystals turned to be $q = (0.9 \pm 0.15)e$ per site along the dislocation line (e is the electron charge). In the impurity crystals investigated by us here, $q \approx 35\ e$/site at $T = 300$ K and at a plastic deformation rate $\dot{h} = 10\ \mu$m/min.

Figure 1 shows the dependence of the dislocation linear charge density on the sample temperature at a constant plastic-deformation rate $\dot{h} = 10\ \mu$m/min. Increasing the temperature leads to a decrease of q, and $q \approx 0.21\ e$/site at $T = 390$ K.

The conductivity of ZnS crystals is determined by carriers of one type—electrons—whose concentration n_e can be easily determined if the dark resistivity ρ is known:

$$n_e = 1/\rho e \mu; \qquad (1)$$

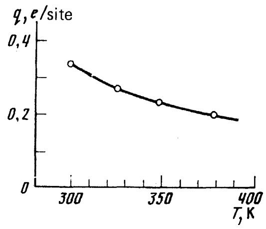

FIG. 1. Temperature dependence of the dislocation linear charge density in ZnS:Cu, Al crystals.

here $\mu \sim 150$ cm²/sec · V is the electron mobility at $T = 300$ K.[11] In the ZnS crystals investigated by us the concentration of the free electrons is $n_e \sim 10^7 - 10^6$ cm^{-3}, and the Debye screening radius r_D turns out to be of the order of 1 mm. The free carriers therefore can not screen the radial electric field E around the dislocation, which has the same geometry with the electric field of a charged filament:

$$E=2q/\varepsilon_0 r, \tag{2}$$

where $\varepsilon_0 \approx 7$ is the dielectric constant of the ZnS crystal and r is the distance from the dislocation core. At a linear dislocation charge density $q=0.34$ e/site the electric field intensity E at a distance $r=10^{-7}$ cm from the dislocation core turns out to be $E=3.4\times10^6$ V/cm.

A stationary electric field of the same intensity, applied to a ZnS sample, causes electrons to tunnel from the centers to the conduction band.[12] Consequently tunneling of electrons from impurity levels and capture centers into the conduction band can occur in ZnS crystals in the electric fields that exist around the moving charged dislocations D. The free electrons produced thereby can radiatively recombine on the produced hole centers C$^+$ and cause the samples to luminesce. This process can be represented schematically in the form

$$D+C\to e+C^+, \quad e+C^+\to C^*\to C+h\nu. \tag{3}$$

3. SPECTRAL AND TEMPERATURE CHARACTERISTIC OF THE PHOTOLUMINESCENCE OF ZnS CRYSTALS

Most investigations were made on ZnS single crystals doped with Cu and having Al as a coactivator. The luminescence spectrum of such a system has been well investigated and depends on the relative and absolute concentrations of the activator Cu and coactivator Al.[13,14] ZhS phosphors show the blue, green and orange-red emission bands of the copper complexes.[14]

The luminescence of copper complexes is produced in accord with the Prener–Williams two-level scheme by electronic transitions in centers made up of clusters of compenstated donors and acceptors. The green and blue emission bands are due to the compensated copper atoms that replace the Zn in the lattice site ($[\mathrm{Cu}^+]_{\mathrm{Zn}^{+2}}$).[15,16] The green emission is due to the transition of an electron from a donor level, e.g., from a nearby Al or Cl atom, to a ($[\mathrm{Cu}^{+2}]_{\mathrm{Zn}^{+2}})^0$ center. The position of the maximum of the green band depends on the type of donor. Thus, $\lambda_{\max}=520$ nm and 527 nm for ZnS : Cu, Cl and ZnS : Cu, Cl, respectively.[14] The blue emission is the result of electron transitions from shallow donor levels near the bottom of the conduction band to the analogous centers ($[\mathrm{Cu}^{2+}]_{\mathrm{Zn}^{+2}})^0$.

The photoluminescence spectrum of ZnS : Cu, Al crystals at various temperatures is shown in Fig. 2. At $T=300$ K the principal maximum in the spectrum, corresponding to the green emission of copper complexes, is located in the 530 nm region. The step at 650 nm corresponds to the orange-red emission, and the broad violet wing of the spectrum corresponds to the blue emission of the copper complexes.

For a detailed study of the photoluminescence spectrum and the DL spectrum, the obtained experimental spectra were subdivided into separate bands in the computer, using a program developed at the Experimental Mineralogy Institute of the USSR Academy of Sciences. The band characteristics obtained from the reduction of the photoluminescence spectrum at $T=300$ K and a comparison of the band positions with the published data are given in the table.

When the temperature is raised, the blue emission is quenched, and at $T=300$ K the photoluminescence spectrum has only two bands, green ($\lambda_{\max}=536$ nm) and orange-red ($\lambda_{\max}=645$ nm) (Fig. 2). The temperature dependence of the intensities of the principal photoluminescence bands of the ZnS : Cu, Al crystal (blue, green, and orange-red) in the temperature region 300–400 K is shown in Fig. 3.

4. MECHANISM OF DEFORMATION LUMINESCENCE. SPECTRAL AND TEMPERATURE CHARACTERISTICS

As already noted,[1,2] plastic deformation of ZnS crystals doped with Cu or Mn and with Al as a coactivator leads to luminescence of the samples during the entire time of the plastic deformation. It was shown in Ref. 2 that stationary DL, in contrast to pulsed deformation electroluminescence,[1,2,3] comes from the volume of the ZnS sample and is connected with excitation of luminescence centers by moving dislocations. Figure 4 shows a plot of the deformation and of the DL of ZnS : Cu, Al single crystals at a constant deformation rate $\dot{h}=10$ μm/min. It is seen that the DL does not occur in the elastic region and appears only in plastic deformation. An increase of the deformation rate causes a proportional growth of the emission intensity.

Figure 5 shows the normalized photoluminescence spectrum of the original ZnS : Cu, Al sample and the DL spectrum at $T=300$ K. The photoluminescence spectrum consists of three copper-complex emission bands: blue,

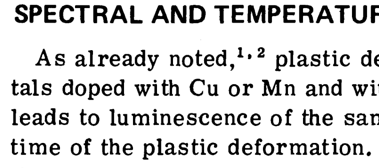

FIG. 2. Photoluminescence spectra of ZnS:Cu, Al crystals at various temperatures: 1—$T=300$ K; 2—$T=330$ K; 3—$T=360$ K; 4—$T=390$ K.

TABLE I.

Luminescence bands	Position, nm	Half-width, eV	Amplitude, rel. un.	Band position λ_{max}, nm
Blue emission of copper complexes	467	0.36	28	467 [17]
Green emission of copper complexes	524	0.46	83	527 [14] 522 [17]
Orange-red emission	645	0.46	17	630 [18]

green, and orange-red at $\lambda_{max} = 467$, 524, and 645 nm, whereas only the green emission of the copper complexes appears in the DL. The DL spectrum is not as rich as the photoluminescence spectrum for reasons discussed below.

The temperature dependence of the intensity of the green DL band at a constant deformation rate $\dot{h} = 10$ μm/min is shown in Fig. 3. It is seen that the DL intensity decreases more rapidly with increasing temperature than the intensity of the green luminescence band.

The onset of DL in ZnS, ZnSe, and CdS crystals can be explained by taking into consideration the presence of electric fields around the moving dislocations. As far back as in 1958, Keldysh has shown[19] that electron-hole pairs are produced in semiconductors in a strong electric field tunneling of the electrons from the valence to the conduction band. A theory of electron tunneling from deep impurity levels into the conduction band in strong electric fields, with account taken of multiphonon processes, was subsequently developed.[20,21]

We examine now the mechanism of excitation of centers when charged dislocations move in a crystal. The electric potential surrounding the dislocations bends the valence band and the conduction band strongly. The electron center "floats up" in synchronism with the band bending as the dislocation core approaches. Starting with a certain distance from the dislocation core, the processes of electron tunneling from the centers into the conduction band become significant.

The electric field intensity E around the dislocation is given by Eq. (2). The potential produced by the dislocation takes therefore the logarithmic form

$$\varphi(r) = \frac{2q}{\varepsilon_0} \ln \frac{r_D}{r}, \tag{4}$$

where r is the distance from the dislocation core. Let the electron center be located at a distance r_1 from the dislocation core. In an approximate treatment of the tunneling of the electron from the center, the problem can be greatly simplified by linearizing the potential near the center. It is assumed here that during the tunneling time the electron is situated in a constant electric field

$$E(r_1) = 2q/\varepsilon_0 r_1. \tag{5}$$

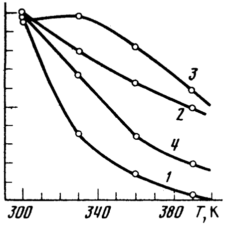

FIG. 3. Temperature dependences of the intensities of the blue (curve 1), green (2), and orange-red (3) photoluminescence bands and of the green band (4) of the deformation emission in ZnS:Cu, Al crystals.

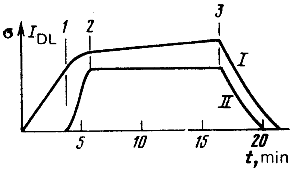

FIG. 4. Intensity of deformation luminescence for deformation with a constant rate $\dot{h} = 10$ μm/min (curve II). Diagram of the deformation (curve I): 1) instant of onset of the DL, 2) the DL reaches a stationary regime, 3) end of active deformation of the crystal.

The expression for the tunneling probality in a constant electric field from an excited state of a center located at a depth $\Delta U_0 - \mathscr{E}$ is of the form[20,21]

$$W(\mathscr{E}) = \frac{eE}{2(2m^* \Delta U_0)^{1/2}} \exp\left\{ -\frac{4}{3} \frac{(2m^*)^{1/2} (\Delta U_0 - \mathscr{E})^{3/2}}{E\hbar e} \right\}. \tag{6}$$

In this case the expression for the per-second probability of electron tunneling from a center located at a depth ΔU_0 below the bottom of the conduction band and at a distance r_1 from the dislocation core takes the form

$$W = \frac{qe}{\varepsilon_0 r_1 (2m^* \Delta U_0)^{1/2} kT} \int_0^{\Delta U_0} \exp\left\{ -\frac{2}{3} \frac{(2m^*)^{1/2} \varepsilon_0 r_1 (\Delta U_0 - \mathscr{E})^{3/2}}{eq\hbar} - \frac{\mathscr{E}}{kT} \right\} d\mathscr{E}. \tag{7}$$

To find the true tunneling probability we must recognize that in plastic deformation the dislocations move with a certain velocity v. Then the probability of excitation of the center by a nearby moving dislocation is

$$W_0(r_0) = \frac{2q}{\varepsilon_0 r_0 (2m^* \Delta U_0)^{1/2} kT}$$

$$\times \int_0^{\infty} \int_0^{\Delta U_0} \exp\left\{ -\frac{2}{3} \frac{(2m^*)^{1/2} \varepsilon_0 (r_0^2 + v^2 t^2)^{1/2} (\Delta U_0 - \mathscr{E})^{3/2}}{eq\hbar} - \frac{\mathscr{E}}{kT} \right\} d\mathscr{E}\, dt, \tag{8}$$

where r_0 is the minimal distance between the dislocation and the center (the impact distance).

At $T = 300$ K and at a plastic deformation rate $\dot{h} = 10$ μm/min the dislocation linear charge density is $q = 0.34$ e/site. The average dislocation velocity in the investigated crystals can be determined from the relation $\dot{\varepsilon} = N_d v_d b / 2\Omega$, where N_d is the number of mobile disloca-

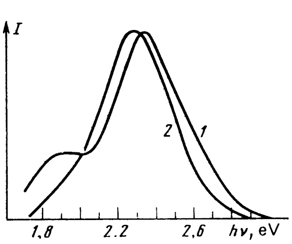

FIG. 5. Photoluminescence (1) and deformation luminescence (2) spectra of ZnS:Cu, Al crystals at $T = 300$ K; $\dot{h} = 10$ μm/min.

tions, b is the Burgers vector, Ω is the sample volume, and $\dot{\varepsilon}$ is the dimensionless rate of the plastic deformation. Assuming $N_d \approx 10^6 - 10^7$ cm^{-2} we obtain at $\dot{h} = 10$ μm/min a dislocation velocity $v_d \approx 5 \times 10^{-4} - 5 \times 10^{-2}$ cm/sec. At these parameter values we calculated the excitation probability $W_0(r_0)$ of the centers as a function of the impact distance and determined the effective radius r_{int} of the interaction with these centers. It is given by the relation

$$r_{\text{int}} = \int_0^\infty W_0^*(r)\,dr, \quad W_0^* = \begin{cases} 1 & \text{at } W_0(r) > 1 \\ W_0(r) & \text{at } W_0(r) \leqslant 1 \end{cases}. \tag{9}$$

It is obvious that the interaction radius is a function of the dislocation linear charge density, of the depth of the trap, of the temperature, and of the dislocation velocity:

$$r_{\text{int}} = F(q(T), \Delta U_0, T, v). \tag{10}$$

Numerical integration of (8) and (9) shows that r_{int} depends little on v and T and is very sensitive to changes of q and ΔU_0 (for example, the interaction radius is 100 and 5 Å for ΔU_0 equal to 0.8 and to 2.75 eV, respectively. Therefore r_{int} decreases rapidly with increasing temperature, since the dislocation charge decreases with increasing T (Fig. 1).

The number of copper complexes excited by the moving dislocations determines the intensity of the experimentally observed DL:

$$I_{\text{DL}} = N_{\text{exc}}\eta = \frac{2\dot{\varepsilon}}{b}\Omega r_{\text{int}} N_{\text{Cu}}\eta, \tag{11}$$

where N_{Cu} is the number of copper complexes per unit volume and η is the quantum yield of the intracenter luminescence. Formula (11) explains readily why the DL intensity decreases with increasing temperature more rapidly than the intensity of the green band in the photoluminescence spectrum. In fact, the temperature dependence of the photoluminescence is determined by the dependence of the quantum yield on the temperature, whereas the DL intensity is determined also by the temperature dependence of r_{int}.

Thus, dislocations motion excites luminescence centers in the immediate vicinity of the dislocation core, at distances of the order of r_{int}. The electron tunnels into the conduction band, where it stays until it recombines on the luminescence spectrum. In such a mechanism we can also expect radiative recombination near the dislocation, i.e., in the strong electric fields produced by the dislocations.

As already noted, the blue emission of the copper complexes has a strong temperature dependence and disappears completely from the luminescence spectrum at $T = 390$ K. The apparent reason is the thermal ejection of the electron from the excited state of the complex into the conduction band. The excited state can also become depleted by electron tunneling into the conduction band in the electric field produced by the dislocation. These processes can explain the absence of the blue band of the copper complexes from the deformation luminescence spectrum. The excited states of the complexes responsible for the green luminescence lie deeper in the forbidden band, therefore their emission is less dependent on the temperature, and ejection of the electrons into the conduction band by the electric field of the dislocation is less effective.

5. INTERACTION OF CHARGED DISLOCATIONS WITH PURPOSELY INTRODUCED ELECTRON CENTERS

To assess the extent to which the premises developed above are universal, it is useful to study the interaction between dislocations and electron centers shallower than $([\text{Cu}^+]_{\text{Zn}^{+2}})^-$. This becomes possible if the investigated samples are exposed beforehand to light of energy $h\nu \sim E_g$.

It is known that illumination of ZnS single crystals with band–band transition ultraviolet leads to storage of the light sum. The holes produced by the light are captured both by the fast capture centers (r centers) and by the copper complexes that appear in the luminescense with formation of $([\text{Cu}^{+2}]^0_{\text{Zn}^{+2}})$ ions. According to the published data[22,23] the electrons are localized on a large number of traps, but at 300 K only the deep donor levels located at $\Delta U_0 \sim 0.7 - 0.8$ eV from the bottom of the conduction band are stable (we shall call them E-centers). Our investigations have shown that the maximum of the thermally stimulated luminescence (TSL) in ZnS:Cu,Al crystals with stored light sum is observed at ~370 K (heating rate ~0.3 deg/sec), and this, according to the data of a number of studies,[22-24] corresponds precisely to release of electrons from the E centers.

When dislocations move in crystals with stored light sum, the electrons from the E-centers should tunnel into the conduction band and their subsequent recombination with holes localized on optically active centers should lead to activator luminescence. Plastic deformation of ZnS:Cu,Al single crystals in which the light sum is stored beforehand is in fact accompanied by a luminescence of intensity more than 1.5 times higher than the DL intensity of the initial sample. The observed increase of the DL is obviously due to emission of the previously stored light sum by the moving dislocations.

It was found possible to determine experimentally the radius of the interaction of the dislocations with the electron E-traps. The total number N_0 of the light quanta emitted when the sample is heated is proportional to the E-center concentration N_e:

$$\Omega N_e = \alpha N_0; \tag{12}$$

where α^{-1} is the TSL quantum yield. After a second storage of the light sum and a plastic deformation of the sample by an amount $\Delta\varepsilon$, the traps are emptied in a fraction $\Delta\Omega$ of the volume. The number of E-centers annihilated by the deformation is $\Delta N = Sr_e N_e$, and since $\Delta\varepsilon = Sb/2\Omega$, we get

$$\Delta N = 2\Omega\Delta\varepsilon r_e N_e / b. \tag{13}$$

After producing the thermal emission, we determine the number N_1 of centers remaining in the sample after partial emission of the light sum as a result of the deformation:

$$\Omega N_e - \Delta N = \alpha N_1. \tag{14}$$

From (12)–(14) we get

$$r_e = \frac{N_0 - N_1}{N_0}\frac{b}{2\Delta\varepsilon}. \tag{15}$$

The values of r_e determined from (15) at $\Delta\varepsilon = 0.75\times10^{-2}$ and 1.25×10^{-2} are respectively 50 and 40 Å. The values of r_e obtained by the method described above (~50 Å) are a lower-bound estimate of the effective radius of the interaction of the dislocations with the E-centers, since it is assumed in the calculations that all the dislocations move along new paths and no account is taken, in general, of the possible overlap of the swept volumes.

The foregoing theoretical estimate of the radius (r_e^t) of the interaction of the dislocations with the E-centers ($r_e^t \sim 10^{-8}$ cm) agrees quite well with the experimentally determined r_e.

6. DRAGGING OF ELECTRONS BY MOVING DISLOCATIONS

As already noted, dislocations that move in a crystal with stored light sum release electrons stored in the E centers in a diameter ~10^{-6} cm. In the volume already swept by the dislocations the electron traps are emptied, so that the electron ejection process takes place only ahead of the moving dislocations. The electrons that land in the conduction band move along the electric field gradient produced by the dislocation and contribute to the current produced when the sample is plastically deformed. As a result, an additional current (dragging current) is produced in a crystal with stored light sum, whose value can be estimated in the following manner.

The volume swept by the moving dislocations per unit time is

$$\Delta\Omega = N_d v R_e.$$

The dragging current is

$$i_{\rm dr} = e v_{\rm eff} \Delta n, \quad \Delta n = \Delta\Omega N_e \tau.$$

This means that

$$i_{\rm dr} = e N_d v R_e N_e \tau v_{\rm eff},$$

where $v_{\rm eff}$ is the effective electron velocity, and $v_{\rm eff}\tau = L$ is the distance covered by the electron prior to recombination with the hole center.

The current produced by the motion of the charged dislocations is

$$i = q N_d v.$$

The ratio

$$\frac{i_{\rm dr}}{i} = \frac{e}{q} R_e N_e L = K_{\rm dr}$$

is the dragging coefficient. It reflects the contribution of the dragging process to the total current i_0 produced when the crystal with stored light sum is deformed ($i_0 = i + i_{\rm dr}$). At $L\sim10^{-4}$ cm, $R_e\sim10^{-6}$ cm, and $N_e\sim10^{16}$ cm^{-3} the dragging coefficient is $K_{\rm dr}\sim0.1$. We used for the estimate the value $L\sim10^{-4}$ cm, which is of the order of the average distance between dislocations.

The experiments have shown that after the light sum is stored in ZnS : Cu, Al crystals the current produced upon plastic deformation increases in fact by 30%. The increase of the current can be explained within the concepts developed in the present article.

We think that it is important to take into account the dragging processes when the true charge of a dislocation is determined, especially when the influence of illumination on the dislocation charge is investigated.[25]

Our investigations allow us to conclude that the charged dislocations moving in ZnS crystals cause a stationary deformation luminescence that proceeds in two stages. In strong electric fields produced by charged dislocations, the electrons localized on traps in activator centers tunnel into the conduction band (first stage of the DL). The recombination of the electrons released by the dislocations with the polarized luminescence centers leads to intracenter luminescence (second state of DL).

We have shown that the release of electrons by charged dislocations that move in the course in plastic deformation and the subsequent motion of the electrons along the electric field gradient produced by the dislocations can contribute to the dislocation current produced when the crystal is loaded.

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Formation of polarization-echo and polarization-avalanche signals in nonpiezoelectric dielectrics

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We develop a quantum-mechanical theory of coherent polarization effects that can arise not only in piezoelectrics but also in all physically inhomogeneous nonpiezoelectric dielectrics. An anharmonic mechanical oscillator coupled with an electric dipole moment is used as the model. It is shown that this model can describe simultaneously both the polarization echo and the polarization avalanche. The polarization avalanche can be illustratively represented as the relaxation of the oscillations of an initially compressed or bent body after the external driving force has been removed. The theory is constructed using the formalism of cyclotron and ferrimagnetic echo, thus demonstrating that all these effects have a common physical character, being concrete representations of one and the same dynamic property of nonlinear physical systems.

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INTRODUCTION

An arbitrary system of weakly interacting particles, excited independently of one another by an external coherent field, can generate under certain conditions superradiant signals of the Bloch-induction,[1] Hahn echo,[2] or boson avalanche[3] type. All these signals are generating by an oscillating macroscopic polarization formed by a set of coherently excited multipoles. This common property of all the induction, echo, and avalanche phenomena can point the way to the search and prediction of new analogous physical effects.

The search for these coherent effects can follow two directions: a) Search for new types of "carriers" that radiate multipoles unconnected with spins but having individual physical properties and definite oscillation eigenfrequencies. Examples of such carriers are powder particles, domain wals, fluxoids, rotons, dislocations, and others, b) Search for multipoles of new physical nature and connected with the spins. The most interesting example of this kind is the discovery of elastic multipoles connected with the electron and nuclear spins and generating spin-phonon echo signals.[4] Of course, greatest interest attaches to observation of new types of radiating multipoles connected with carriers of a new type.

By now, echo-type signals have been observed in such physical objects as ferrimagnetic powders[5] and ferroelectric and piezoelectric powders (see, e.g., Ref. 6–8). The echo signals in powders are due to oscillating polarization of the electric dipoles that are either spontaneously present in the sample (ferroelectrics), or result from piezoelectric coupling (piezoelectrics). These phenomena were named "polarization echo" (PE).

We show in this paper that PE can be observed in a large new class of powdered materials—powdered centrosymmetric dielectrics. The piezoelectric properties of centrosymmetric dielectrics are the result of the inhomogeneous distribution of the charge in a layer near the surface. These dielectric will be called hereafter "local piezoelectrics."

It has become obvious, following the publication of Ref. 9, that echo-type signals can be observed in two principally different quantum systems: of the spin type, wherein the energy spectrum of each particle is bounded, and of the oscillator type, where the spectrum of an individual particle is equidistant and not bounded from above. This result found a general theoretical explanation in terms of abstract Lie algebras. It has turned out that echo signals arise whenever an algebra that described the unified properties of an external generator and of a quantum system becomes unsolvable. As to echo of the spin type (STE) or of the oscillator type (OTE), it can be expressed in terms of concrete representations of abstract unresolvable Lie algebra. The OTE has a number of important and interesting features compared with STE: under certain conditions the signal increases without limit with increasing excitation; ac-