A model of ferroelectric ordering in nonlinear proustite crystals (Ag_3AsS_3)

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We propose a model based on the existence of a strong coupling between the dipole, phonon, and electron subsystems near the ferroelectric phase transition point, which can describe the experimentally observed basic singularities of the phase transition in proustite under the influence of light.

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In recent experimental studies (see Refs. 1, 2, and their references) it was disclosed that the properties of the ferroelectric phase in proustite vary sharply as a result of the action of light on the crystal in the temperature region near the phase transition point ($T_c = 26.7$ K). This greatly increases the dielectric of the ferroelectric phase compared to the case in which there is no action of light on the crystal near the transition point. It is characteristic that the crystal "remembers" the effect of the action of light: after once being irradiated by light near the transition point and kept at room temperature for an extended time, the crystal exhibits the same anomalies of the dielectric properties during the transition to the ferroelectric phase without a new action of light. At the same time, the heating of the crystal to an adequately high temperature destroys the indicated anomalous properties. Note that such behavior has so far been observed only in proustite.

The microscopic mechanisms, which produce such effects, are certainly worth studying. In particular, a correct understanding of such mechanisms should facilitate the search for other objects having the same properties as proustite.

To construct a microscopic model we must first note that at $T \gg T_c$ the concentration of electrons in the conduction band must be small. The action of light leads to the appearance of additional free carriers, which markedly increases the conductivity.[1,2] We emphasize that the generation of free carriers by light in proustite can also be observed at room temperature.[3]

It should be pointed out that to correctly understand the mechanisms of low-temperature generation of free carriers, we must investigate the dependence of the intensity of such generation on the intensity of light and on wave lengths of the incident light. Unfortunately, these problems were not investigated in the experiment.

The ordering of dipoles as a result of transition to the ferroelectric phase is accompanied by a lattice distortion due to the dipole-phonon interaction. In turn, the condensation of the soft phonon mode in this transition due to the electron-phonon interaction rearranges the electronic spectrum of the system. Thus, it is natural to assume that the electron and dipole subsystems are related through the lattice.

Taking this fact into account, we choose the model Hamiltonian of the system under consideration in the form

$$H = H_{ph} + H_e + H_{e-ph} + H_d + H_{d-ph} \,. \tag{1}$$

Here the first term describes the energy of the free phonons, the second term describes the energy of the free electrons, and the third term describes the Frolich electron-phonon interaction.[4] The energy operator of the dipole subsystem has the form

$$H_d = -\sum_{m,n} \Lambda_{mn} \sigma_m^+ \sigma_n^- \,, \quad \sigma_m^{\pm} \equiv \frac{1}{2}(\sigma_m^x \pm i\sigma_m^y) \,, \tag{2}$$

where summing is carried out over all the N_d dipoles. It is assumed that the number of electrons is comparable to that of the dipoles: $N_d = \alpha N_e$. For simplicity, we assume that the dipole-dipole interaction is long range: $\Lambda_{mn} = \lambda_{mn}/N_d$, where λ_{mn} is a bounded function.

The dipole-phonon interaction operator in the linear approximation with respect to the dipole shift has the form[5]:

$$H_{d-ph} = -\frac{1}{\sqrt{N_d}} \sum_{m,n} A_{mn}(q)\, \sigma_m^+ \sigma_n^- (b_q + b_{-q}^+) \,, \tag{3}$$

where $b_q (b_q^+)$ is the phonon operator of the qth mode which causes the instability of the lattice.

The last two terms in Eq. (1) described the phase transition to the state characterized by dipole ordering. The dipole order parameter (specific polarization) is determined by the equation

$$P = \frac{1}{2} \operatorname{th} \frac{(\lambda_0 + A_0(q) P^2) P}{kT} \,, \quad \lambda_0 \equiv \frac{1}{N^2} \sum_{n,m} \lambda_{nm} \,,$$

whose solutions are given in Fig. 1. As can easily be seen, depending on the ratio of the parameters of the dipole-dipole λ_0 and the dipole-phonon $A_0(q)$ interaction, the phase transition can be either a second- or a first-order transition, consistent with the experiment[1,2]; whereupon, the temperature of the first-order transition is higher than that of the second-order transition.

During transition to the state with a dipole ordering in the dipole subsystem, a macroscopic condensation of the soft phonon mode q occurs in the phonon subsystem.[5] The electronic subsystem, in turn, can also have a phase transition characterized by a macroscopic occupation of the phonon mode (the Frolich-type Hamiltonian with a single resonance mode of the phonon field is examined). For simplicity, we assume that the condensed mode is also a q mode. The phase transition in the electronic subsystem is characterized by the rearrangement of the electronic spectrum and the appearance of the forbidden gap, which can be described in terms of the modified method of approximating Hamiltonians.[6] This determines the dielectric properties of the system. The induced gap is determined by

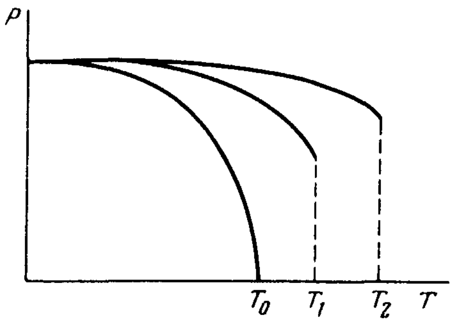

FIG. 1. Temperature dependence of the specific polarization P. The point T_0, T_1, and T_2 correspond to the second- and first-order transitions.

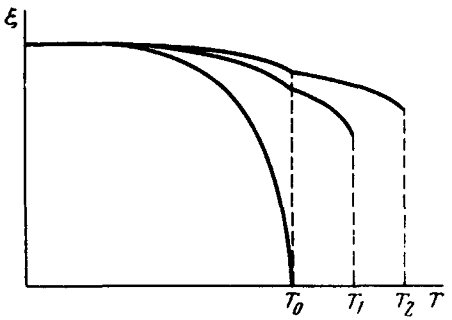

FIG. 2. Temperature dependence of the coherent lattice distortion.

$$E = \frac{J^2}{\omega_q}\sqrt{\xi}, \quad \xi = \frac{\langle b_q^+ \, b_q \rangle}{N_d},$$

where J is the coupling constant in the Hamiltonian H_{e-ph}.

The coherent distortion of the lattice is determined by the relation

$$\xi = A_0(q)\,P^2 + \left(\frac{J^2}{\omega_q}c\right)^2, \quad c = \frac{1}{2N_d}\sum_p \operatorname{th}\frac{\sqrt{\epsilon_p^2 + \frac{J^4}{\omega_q^2}c^2}}{2kT}.$$

Its temperature dependence is given in Fig. 2.

Thus, the model under consideration can describe the ferroelectric ordering of dipoles and a simultaneous variation of the dielectric properties in proustite due to the action of light. The model does not explicitly include the term describing the light generation of the free carriers. To correctly select such a term we must determine the aforementioned dependences of generation on the parameters of the incident light.

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