Pressure effect on the ferroelectric ordering in the framework of the Blume–Emery–Griffiths model

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Abstract

The effects, taking place under external pressure, are investigated in the framework of the Blume–Emery–Griffiths (BEG) model corresponding to the local potential with three minima. The deformable BEG (d-BEG) model is proposed for this purpose; it is taken into consideration that the influence of mechanical stress is realized through the lattice strain resulting in restructuring of local atomic configurations. Based on this model, the pressure dependences of the $u = \Delta V/V$ volume deformation are calculated on an example of the $Sn_2P_2S_6$ crystal. The presence of anomalies of $u(p)$ function in the regions of ferroelectric phase transitions of the first and second order as well as the tricritical point is established; the behaviour of the volume compressibility in these cases is investigated. Obtained results are in agreement with the experimental data.

1. The BEG model, $Sn_2P_2S_6$ and pressure

Lattice models well describe the order-disorder phase transitions in the crystals with locally anharmonic structure elements. In the case of the three-well symmetrical potential an appropriate one corresponds to the Blume–Emery–Griffiths (BEG) model [Blume M., 1971]. The model can be applied to description of crystals belonging to the $Sn_2P_2S_6$ family (with the possible partial substitutions Sn → Pb and S → Se, see [Vysochanskii Yu.M., 2006]) which are an example of such objects.

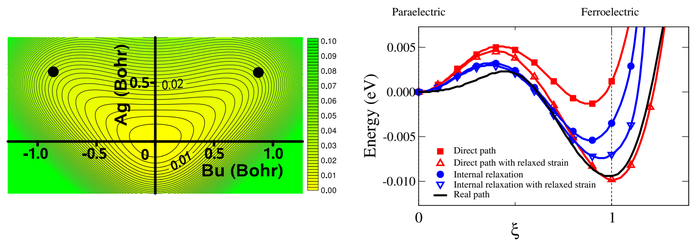

Figure 1: *Results of calculations within LDA for $Sn_2P_2S_6$ [Rushchanskii K.Z., 2007]: (left) frozen-phonon energy surface (in eV) for a linear combination of A_g and B_u mode amplitudes (black circles denote the projections of the positions of the global FE minima) and (right) energy profile along the valley lines.*

The performed *ab initio* calculations [Rushchanskii K.Z., 2007] showed that ionic groups P_2S_6 exist in three configurations (determined by their form and distribution of electronic charge), which in the paraelectric phase are described by a symmetrical three-well potential in the energy space. In the absence of external influence, the $Sn_2P_2S_6$ crystal exhibits the second order phase transition to the ferroelectric phase at $T_c = 337$ K due to a dipole ordering of these groups [Yevych R.M., 2011].

The thermodynamics of the crystal is sensitive to the external hydrostatic pressure and to the partial substitutions Sn → Pb and S → Se. At the increase of pressure the temperature T_c of the second order phase transition decreases, a tricritical point is achieved at $T_{TCP} = 220$ K and the ferroelectric state is suppressed at $p = p^* = 1.5$ GPa [Vysochanskii Yu.M., 2006]. This effect can be explained by the influence of the pressure on the Δ parameter.

2. The model

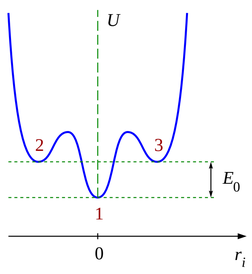

Figure 2: A three-well local potential (states $|1\rangle$, $|2\rangle$, and $|3\rangle$) and a definition of the energy parameter E_0.

Let us start from the Hamiltonian $\hat{H}$ of the lattice model where three states $|1\rangle$, $|2\rangle$, and $|3\rangle$ (with respective energies E_1, E_2 and E_3) are possible for each site. In the representation of Hubbard operators ($X_i^{\alpha\beta} = |i,\alpha\rangle\langle i,\beta|$) one has

$$\hat{H} = \sum_i \sum_{\alpha=1}^{3} E_\alpha X_i^{\alpha\alpha} + \hat{H}'. \quad (1)$$

Operators $X_i^{\alpha\alpha}$ project on the states $|i,\alpha\rangle$ so their average values $\langle X^{\alpha\alpha}\rangle$ are equal to occupations of these states. Then, the single-site part can be written down as

$$\hat{H}_i = -\frac{h}{2}(X_i^{33} - X_i^{22}) + E_0(X_i^{33} + X_i^{22}) \equiv -hS_i^z + E_0 n_i, \quad (2)$$

where h is the field conjugated to the dipole moment, $E_0 = E_2^{(0)} - E_1 = E_3^{(0)} - E_1$ is the difference of energies of the side and central configurations at $h = 0$, $S_i^z = (X_i^{33} - X_i^{22})/2$ (related to the local dipole moment) and $n_i = X_i^{33} + X_i^{22}$ (that determines an occupancy of side positions). It should be mentioned that for every lattice site a condition $\sum_{\alpha=1} X_i^{\alpha\alpha} = 1$ is fulfilled. The interaction part $\hat{H}'$ of the Hamiltonian of the model can be written in general in the form

$$\hat{H}' = -\frac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z - \frac{1}{2}\sum_{ij} K_{ij} n_i n_j. \quad (3)$$

Deformation of the crystal lattice is an immediate reason of variation of local potentials (i.e., E_0):

$$\hat{H}'' = D\sum_i (X_i^{33} + X_i^{22})u + \frac{N}{2} v c_0 u^2, \quad (4)$$

taking into account the renormalization due to deformation $E_0 \to \tilde{E}_0 = E_0 + Du$ (here $u = \Delta V/V$ is a relative change of the volume) as well as the energy of an elastic deformation (c_0 is the volume elastic constant, v is the volume related to the one formula unit, N is the number of relevant elements), while D is the constant of an electron-deformational interaction.

An equilibrium value of the u parameter in the presence of the $\hat{H}''$ interaction can be obtained starting from the condition of a thermodynamic equilibrium $\partial G/\partial u = 0$, where G is the Gibbs free energy derived from the Helmholtz free energy $G = F - Nvu\sigma$, where σ is a mechanical stress. Here F is a characteristic function of (T, V, N) (in our case, of (T, u, N)) variables, while the Gibbs free energy G is a function of (T, σ, N). Since $\partial G/\partial u = \partial F/\partial u - Nv\sigma = \langle \partial \hat{H}/\partial u\rangle - Nv\sigma$, a deformation u is connected with the external mechanical stress as

$$c_0 u + (D/v)\langle X_i^{33} + X_i^{22}\rangle = \sigma \quad (5)$$

(assuming an absence of a modulated ordering). Condition (5) is an exact relation which can be considered as the generalized Hooke's law: the role of the external stress σ is not limited only to the deformation of the lattice, the stress also affects the occupations of the side positions ($\bar{n} = \langle X^{22} + X^{33}\rangle$) of local wells.

The deformation u can be eliminated using equation (5). As a result, the Hamiltonian of our model can be rewritten as

$$\hat{H} = \sum_i \left(E_0 + \frac{D}{c_0}\sigma\right) n_i - \frac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z - \frac{D^2}{vc_0}\sum_i \bar{n} n_i + U, \quad (6)$$

$$U = \frac{N}{2c_0} v\sigma^2 - \frac{ND}{c_0}\sigma\bar{n} + \frac{N}{2}\frac{D^2}{vc_0}\bar{n}^2. \quad (7)$$

The third term in expression (6) has a form corresponding to the energy of a local quadrupole in the mean field $K_{\text{eff}}\bar{n}$, where the constant of the effective quadrupole interaction equals to $K_{\text{eff}} = D^2/(vc_0)$. The role of the stress σ is not limited to the appearance of the field $(D/c_0)\sigma$ acting directly on quadrupoles. It is also manifested in appearance of some additional terms in expression (7). Equivalence to the BEG Hamiltonian is achieved only in the absence of external stresses (at $\sigma = 0$).

3. Thermodynamics in the MFA

The model described by the Hamiltonian

$$\hat{H} = \sum_i \hat{H}_i + \hat{H}' + \hat{H}'', \quad (8)$$

can be named as the deformed BEG model (d-BEG). At $K_{ij} = 0$ one can obtain in the mean field approximation (MFA)

$$\hat{H}_{\text{MF}} = \frac{N}{2}J\eta^2 + \frac{N}{2}vc_0u^2 + \sum_i \left[(H + \tilde{E}_0)X_i^{22} + (-H + \tilde{E}_0)X_i^{33}\right]. \quad (9)$$

Here $H = J\eta/2$ (where $J = \sum_j J_{ij}$) is the effective field acting on dipoles, $\eta = \langle S_i^z\rangle$ is the parameter of the dipole ordering that determines the polarization of the system.

Starting from the single-site partition function, we obtain the following expression for the Helmholtz free energy

$$F_{\text{MF}} = \frac{N}{2}J\eta^2 + \frac{N}{2}vc_0u^2 - N\Theta \ln\left(1 + 2e^{-\beta\tilde{E}_0}\cosh\beta H\right), \quad (10)$$

where $\beta = 1/\Theta = 1/k_BT$. Conditions of an extremum of the function $G_{\text{MF}} = F_{\text{MF}} - Nvu\sigma$ result in this case in the equations

$$\eta = \frac{e^{-\beta\tilde{E}_0}\sinh\beta H}{1 + 2e^{-\beta\tilde{E}_0}\cosh\beta H}, \qquad c_0u + \frac{D}{v}\frac{2e^{-\beta\tilde{E}_0}\cosh\beta H}{1 + 2e^{-\beta\tilde{E}_0}\cosh\beta H} = \sigma. \quad (11)$$

The second equation coincides with the earlier obtained relation (5) between the deformation u and the mechanical stress σ thus being a generalization of the Hooke law.

4. Phase diagrams of the deformed BEG model

Starting from the data for $Sn_2P_2S_6$ [Vysochanskii Yu.M., 2006; Bilanych R., 2014], we have fitted the following values of parameters for the deformed BEG model (d-BEG): $v = 0.23 \cdot 10^{-24}$ cm^3, $c_0 = 5 \cdot 10^{11}$ erg/cm^3, $D = -1.1$ eV, $c_0v = 71.8$ eV, $E_0 = -0.011$ eV, $V_{\text{eff}} = 0.017$ eV. The parameter D was calculated using the definition $D = \partial\tilde{E}_0/\partial u$ based on the estimation of the derivative $\partial\tilde{E}_0/\partial p = -\tilde{E}_0/\partial\sigma \approx 0.011 \ldots 0.025$ eV/GPa according to the results of *ab initio* calculations [Yevych R., 2016] (here $p = -\sigma$ is a hydrostatic pressure). The value of the parameter J is chosen from the condition of an optimal fit of the critical temperature T_c at $p = 0$ comparing to its experimental value ($T_c|_{\text{exp}} = 337$ K). The value of $E_0 = -0.011$ eV corresponds to the data presented in [Yevych R., 2016] for a zero pressure.

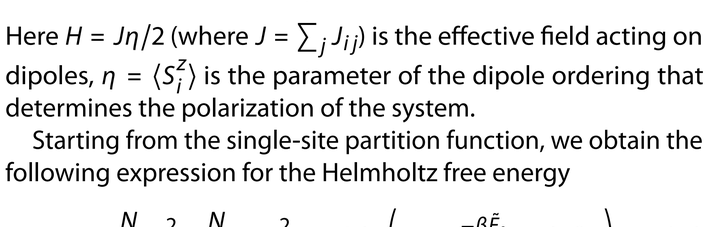

Figure 3: *Dependence of the temperature of the ferroelectric-paraelectric phase transition between the ferroelectric (F) and paraelectric (P) phases (left) on the energy parameter E_0 (at $p = 0$) and (right) on the applied pressure p (at $E_0 = -0.011$ eV) at $J = 0.14$ eV, $c_0v = 71.8$ eV, $D = -1.1$ eV, $V_{\text{eff}} = 0.017$ eV.*

At rise of E_0, the T_c decreases, the order of the phase transition changes at the tricritical point ($E_0|_{TCP} \approx 0.02$ eV) and the ferroelectric (F) phase is suppressed at $E_0 \geqslant 0.026$ eV (figure 3). The temperatures $T_c(p = 0)$ and T_{TCP} as well as the pressure p^* (at which the temperature of the phase transition tends to zero) are relatively close to the experimental data ($T_c|_{\text{calc}}(p = 0) = 330$ K, $T_{TCP}|_{\text{calc}} = 203$ K and $p^*|_{\text{calc}} = 1.7$ GPa while $T_c|_{\text{exp}}(p = 0) = 337$ K, $T_{TCP}|_{\text{exp}} = 220$ K and $p^*|_{\text{exp}} = 1.5$ GPa).

The deformation Δu jumps at the first order phase transition accompanied by compression of the lattice (figure 4). As this takes place, a relative change of the volume $\Delta V/V$ attains to values −0.011 corresponding to the measured change of the unit cell volume for the $Sn_2P_2S_6$ crystal (according to [Vysochanskii Yu.M., 2006], $v_{\text{cell}} \approx 0.457 \cdot 10^{-24}$ cm^3 for the ferrophase ($T = 293$ K) and $v_{\text{cell}} \approx 0.452 \cdot 10^{-24}$ cm^3 for the paraphase ($T = 358$ K)).

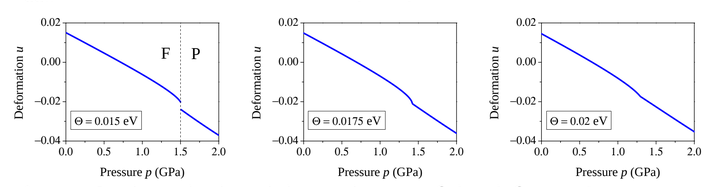

Figure 4: *The calculated dependences of the deformation parameter u on the pressure p at various temperatures (174 K, 203 K and 232 K, respectively); here and in figures 5, 6 and 7: $J = 0.14$ eV, $c_0v = 71.8$ eV, $D = -1.1$ eV, $E_0 = -0.011$ eV, $V_{\text{eff}} = 0.017$ eV.*

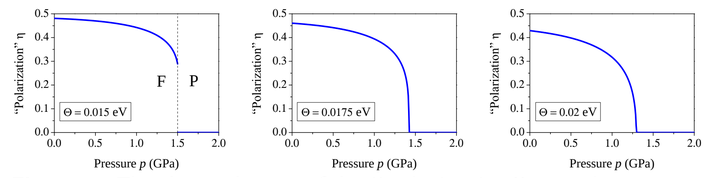

Figure 5: *The dependences of the ''polarization'' η on the pressure p at various temperatures (174 K, 203 K and 232 K, respectively).*

In the tricritical point, the function $\chi(p)$ diverges while nearby this point it demonstrates a peak-like behaviour. Variation of the compressibility within the peak region is of the order of 0.02–0.04 GPa^{-1} (close to the measured values [Slivka A.G., 1999]).

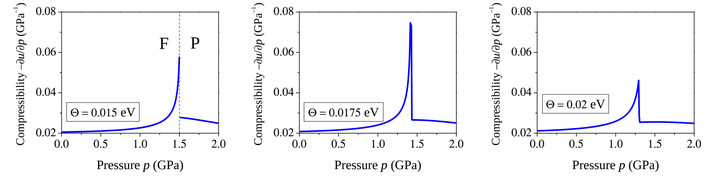

Figure 6: *The dependences of the compressibility χ on the pressure p at various temperatures (174 K, 203 K and 232 K, respectively).*

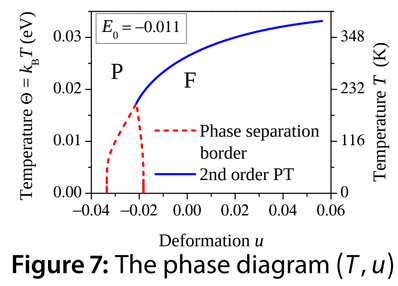

Figure 7: The phase diagram (T, u) for the case of the mechanically clamped crystal (regime u = const).

We can also consider the case of the mechanically clamped crystal (regime u = const). The jump of u at the first order phase transition in the free crystal corresponds to a respective interval of u values located between the paraphase and ferrophase in the case of the clamped crystals (figure 7). Binodals, depicted by dashed lines, were obtained by comparing the Gibbs free energy of both phases and using the deformation jump data along the first order phase transition line in the (u, p) plane. For all values of u and T from the intermediate region (located between areas of the P and F phases) a separation into differently strained fragments of the P and F phases occurs according to the rule $x_P = (u - u_F)/(u_P - u_F)$ and $x_F = (u_P - u)(u_P - u_F)$, where $x_{P,F}$ are the relative fractions of the P (F) phase, $u_{P,F}$ are the values of the deformation u on the respective boundary of the mentioned interval.

5. Conclusions

In the framework of the d-BEG model, the interaction of energy states of the mentioned structure elements (e.g., groups P_2S_6 for the $Sn_2P_2S_6$ crystal) with the lattice deformation leads to the anomaly of the $u(p)$ dependence in the vicinity of the phase transitions from the ferroelectric (F) to paraelectric (P) phase. The lattice compresses and the deformation has a jump Δu at the first order phase transition and changes continuously at the second order one. A peak-like behaviour of the $\partial u/\partial p$ function in the vicinity of the phase transition is also revealed. This peak increases approaching the tricritical point where the compressibility $\chi = -\partial u/\partial p$ diverges. Such behaviour of $u(p)$ and $\chi(p)$ coincides with the observed one.

Thermodynamics of $Sn_2P_2S_6$ is also considered in the case of a clamped crystal (regime u = const). As is shown, at $T < T_{TCP}$ the region of deformation values is present in this regime, where the crystal exists in a mixed state being separated into differently strained fragments of the P and F phases. This mixed phase is located between the ''pure'' P and F phases on the (T, u) phase diagram. Such a state of the phase coexistence can be experimentally identified by measurement of the compressibility $\chi(u)$ in the ''clamped'' regime in the area of the mixed state (here $\chi(u)$ is a linear function on u in the interval $[u_P, u_F]$).