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MICROSCOPIC THEORY OF FERROELECTRIC PHASE TRANSITIONS INDUCED BY ELECTRON-PHONON INTERACTION IN $A^{IV}B^{VI}$-TYPE COMPOUNDS. 2

(Presented by V. Hizhnyakov)

The coefficients of the electron-phonon anharmonicity for stabilizing tetragonal, rhombic and rhombohedral phases in $A^{IV}B^{VI}$-type semiconductors have been calculated. It is shown that in $\overset{IV}{A}_{1-x}\overset{IV}{B}_x\overset{VI}{C}$ systems with the inversion of electronic bands the dependence of T_c on x may be nonmonotonic, passing through the maximum. A comparison with the experiment of the theory developed in this paper (Part 1 and 2) is made for GeTe, PbTe and $Pb_{0.93}Sn_{0.07}Se$, and their parameters are determined.

1. Calculation of the Coefficients of the Vibronic Anharmonicity and other Characteristics of FPT

The coefficients of the electron-phonon anharmonicity of free energy (1.11) (for notations, see Part 1), calculated with the allowance made for (1.36), are expressed as follows

$$\beta_1-\eta_{1ph}=2\Big\{N_0K_0\bar{K}_0I_1-2N_0K_0(\bar{p}_\parallel^2I_2+\bar{p}_\perp^2I_3)+$$

$$+\frac{5}{12}\Big[\frac{4}{3}(p_\parallel\bar{p}_\parallel)^2I_4+8(p_\parallel\bar{p}_\perp)^2I_7+\frac{1}{3}(p_\perp\bar{p}_\perp)^2(5I_5+8I_6)\Big]\Big\},\qquad(2.1)$$

$$\beta_2-\eta_{2ph}=\frac{1}{2}(\beta_1-\eta_{1ph}+N_0K_1\bar{K}_1I_1)-N_0K_1(2\bar{p}_\parallel^2I_2-\bar{p}_\perp^2I_3)+$$

$$+\frac{10}{9}\Big[(p_\parallel\bar{p}_\parallel)^2I_4+(p_\perp\bar{p}_\perp)^2\Big(\frac{5}{4}I_5-7I_6\Big)-3(p_\perp\bar{p}_\parallel)^2I_7\Big],\qquad(2.2)$$

where

$$p_{\parallel,\perp}=\bar{\mathfrak{T}}_{\parallel,\perp}V_{\parallel,\perp};\quad \bar{p}_{\parallel,\perp}=\bar{\mathfrak{T}}_{\parallel,\perp}\bar{V}_{\parallel,\perp};\quad \bar{K}_{0,1}=\frac{N}{n}K_{0,1}\qquad(2.3)$$

and (the quantity I_6 will be calculated numerically)

$$I_1=U_0\varepsilon_0^3(d_1+\nu_1),\quad I_{2,3}=U_0\varepsilon_0^5(d_{2,3}+\nu_{2,3}),\qquad(2.4)$$

$$I_{4,7,5}=U_0\varepsilon_0^7(d_{4,5,6}+\nu_{4,5,6}),\quad I_6=\sum_{\mathbf{k}}E_{\mathbf{k}}^7(k_xk_y)^2.\qquad(2.5)$$

In formulae (2.4) and (2.5)

$$d_1=-C_{1,2}^{-1}L_1^{(1,2)},\qquad d_2=-\frac{C_{1,2}^{-3}}{3}m_3,\qquad(2.6)$$

$$d_3=d_1\mp\varkappa^{-2}d_2+n_1; \qquad d_4=-\frac{C_{1,2}^{-5}}{5}m_4, \tag{2.7}$$

$$d_5=\pm d_2-\varkappa^{-2}d_4+n_2, \quad d_6=d_1\mp2\varkappa^{-2}d_2+$$

$$+2n_1+\varkappa^{-4}d_4-2\varkappa^{-2}n_2-\frac{1}{5}\left(\frac{\Delta^2}{\bar{E}_1}\right)^2C_{1,2}^{-1}\Lambda^{-4}m_5, \tag{2.8}$$

at this

$$m_3=-\delta_{1,2}^{-1}+L_1^{(1,2)}, \qquad m_4=m_3\mp\frac{1}{3\delta_{1,2}^3}, \tag{2.9}$$

$$m_5=2\delta_{1,2}^{-1}-L_1^{(1,2)}+m_4, \quad n_1=\frac{\Delta^2}{3\bar{E}_1}(C_{1,2}\delta_{1,2}\Lambda^2)^{-1}, \tag{2.10}$$

$$n_2=\frac{\Delta^2}{15\bar{E}_1}\Lambda^{-2}(C_{1,2}\delta_{1,2})^{-3},$$

$$\begin{gathered}\nu_1=\varkappa L_2, \quad \nu_2=\frac{\varkappa^3}{3}(-\delta_3^{-1}+L_2), \quad \nu_3=\frac{2}{3}\nu_1,\\ \nu_4=\frac{\varkappa^5}{5}\left(\frac{3\nu_2}{\varkappa^3}-\frac{1}{3\delta_3^3}\right), \quad \nu_5=\frac{2}{5}\nu_2, \quad \nu_6=\frac{8}{15}\nu_1.\end{gathered} \tag{2.11}$$

For $s_1=s_2$ ($\gamma_{10,20}=0$) we have

$$d_1=-\Lambda^{-1}; \quad d_2=-\frac{1}{9\Lambda^3}, \quad d_3=d_1-3d_2\left(\frac{1}{3\varkappa^2}+\frac{\Delta^2}{\bar{E}_1}\right), \tag{2.12}$$

$$d_4=-\frac{1}{25\Lambda^5}, \quad d_5=d_2-5d_4\left(\frac{1}{5\varkappa^2}+\frac{\Delta^2}{3\bar{E}_1}\right), \tag{2.13}$$

$$d_6=\Lambda^{-1}\left\{-1+\frac{2}{9}\Lambda^{-2}\frac{(d_1-d_3)}{d_2}-\frac{\Lambda^{-4}}{5}\left[\frac{1}{5\varkappa^4}+\left(\frac{\Delta^2}{\bar{E}_1}\right)^2+\frac{2\varkappa^{-2}\Delta^2}{3\bar{E}_1}\right]\right\}. \tag{2.14}$$

In case of a degenerate semiconductor in (1.42)—(1.52) and (2.1)—(2.14), the dependence of the squared soft-mode frequency α_1 and the coefficients of anharmonicity $\beta_{1,2}$ on the carrier concentration may be taken into account approximately by the substitution $\Delta\rightarrow\Delta+2E_F$, where the Fermi level is counted from the edge of the corresponding band.

Taking into account the contribution from the dynamical part of the electron-phonon interaction $\varepsilon_{\text{dyn}}^{(1,2)}$ [1] to α_1 and $\beta_{1,2}$, we introduce the effective gap $\bar{\Delta}$ between the initial bands $\varepsilon_\sigma(\mathbf{k})$, analogously to [2,3]. Then the term $\Delta_1=\sum_{\mathbf{q},j}V(\mathbf{q},j)\operatorname{cth}\frac{\hbar\omega_{\mathbf{q}j}}{2k_BT}$ ($V(\mathbf{q},j)$ is determined by constants of vibronic interactions and $\bar{\Delta}$ [1]) is added to Δ. When $2k_BT\gg\hbar\omega_{\mathbf{q}j}$, the quantity $\Delta_1\approx V_0k_BT$. In the case of a simple two-band model, while taking into account only the interband electron-phonon interaction, the contribution Δ_1 to the soft-mode frequency coincides with the one obtained in [3,4]. At this the coefficient V_0 has the same sign as $B_g=\frac{\partial E_g}{\partial T}$ [1] at $T>T_c$ (E_g is the forbidden gap), but $|V_0|<|B_gk_B^{-1}|$.

The Curie point of the second-order FPT is found from the condition $\alpha_1(T_c)=0$, which at $\bar{A}\neq 0$ has the following form:

$$k_B T_c=\frac{M\omega_0^2}{\bar{A}}\left[\tau(T_c)-1\right], \tag{2.15}$$

where

$$\tau(T_c)=\frac{8}{3M\omega_0^2}\left\{\bar{V}_{\perp}^2\left[2i_1(T_c)-\bar{\mathfrak{J}}_{\perp}^2 i_{1\perp}(T_c)\right]+\bar{V}_{\parallel}^2\left[i_1(T_c)-\bar{\mathfrak{J}}_{\parallel}^2 i_{1\parallel}(T_c)\right]\right\}. \tag{2.16}$$

If $V_0=0$, the quantity τ is independent of T_c and (2.15) represents the formula for T_c. When $\bar{A}=0$ T_c is determined by the equation

$$\tau(T_c)=1. \tag{2.17}$$

The solutions of (2.15) and (2.17), $T_c>0$, correspond to FPT, and $T_c<0$, to the potential ones.

From (1.41) it follows that for FPT to occur in $A^{IV}B^{VI}$ compounds the following condition must be fulfilled:

$$\tau(T)>\left(\frac{\hat{\omega}_0(T)}{\omega_0}\right)^2. \tag{2.18}$$

The interband vibronic interaction induces tetragonal, rhombic and rhombohedral phases if

$$L>0; \quad K>0, \tag{2.19}$$

$$L=0, \quad K>0 \tag{2.20}$$

and

$$L<0, \quad L+\frac{K}{16}>0, \tag{2.21}$$

respectively. An analysis shows that the stabilization of rhombic and rhombohedral phases (assuming $\eta_{1,2ph}=0$) is possible only in the presence of **kp** interactions and the anisotropy of energetic spectra of valence and conduction bands.

2. Estimation of the Parameters of the Theory and Comparison with the Experiment

Now the developed theory will be applied to some $A^{IV}B^{VI}$ ferroelectric-semiconductors viz. GeTe, PbTe and $Pb_{0.93}Sn_{0.07}Se$. The numerical values of the parameters of the theory are determined in the following manner. The constants of the interband electron-phonon interaction for GeTe are found in [1] from the temperature dependence of the forbidden gap E_g, including the strain-induced effects. For PbTe and $Pb_{0.93}Sn_{0.07}Se$ the constants $V_{\parallel,\perp}$ are estimated from the experimental values $B_g=\frac{\partial E_g}{\partial T}$ [5] by using the formulae given in [1], whereas $V_{\parallel}\approx V_{\perp}$. The constants $\bar{A}$ and V_0 are estimated from the temperature dependence of the soft-mode frequency in the paraphase $\Omega_{hs}^2=M^{-1}\bar{A}_0 k_B(T-T_c)$ [6]. Using the experimental values of the parameters of electronic spectra $m_{\perp,\parallel}$, $m'_{\perp,\parallel}$, $P_{\perp,\parallel}$, Δ [6–9] and $N=2N_0$, basing on formulae (1.34), (1.37), (1.39); (1.40); we have calculated the quantities $\bar{\alpha}_{10,20}$, $\gamma_{10,20}$ and $\bar{\mathfrak{J}}_{\parallel,\perp}^2$ (the lattice

The compound	$\overline{\mathfrak{T}}^2_{\parallel}$, (eV)^2	$\overline{\mathfrak{T}}^2_{\perp}$, (eV)^2	$\overline{\alpha}_{10}$, eV	$\overline{\alpha}_{20}$, eV	γ_{10}, eV
GeTe (1)	0.0185	0.0927	2.875	0.5752	0
PbTe (2)	1.2496	13.327	170.76	19.99	0
$Pb_{0.93}Sn_{0.07}Se$ (3)	0.8695	1.097	6.555	0.6555	—0.8029
	γ_{20}, eV	$\Delta+2E_F$, eV	$\bar{A}$, (nm)$^{-2}$	V_0	$\bar{V}_{\parallel} \approx \bar{V}_{\perp}$, eV/nm
1	0	0.2	20	0	1.4
2	0	0.187	0	0.225	4
3	0.1338	0.077	0	0.1	4
	$M\omega_0^2$, eV/(nm)^2	$M \cdot 10^{25}$, kg	$\omega_0 \cdot 10^{-12}$, Hz	$\bar{A}_0$, (nm)$^{-2}$	T_c, K
1	33.911	0.77	8.40	20	670
2	52.062	1.31	7.979	20	—70
3	63.904	0.94	10.436	16	—500

constants $a=0.602$, 0.646, 0.612 nm for GeTe, PbTe and $Pb_{0.93}Sn_{0.07}Se$, respectively). Then by formulae (2.15), (2.16) the initial phonon frequencies ω_0 were calculated by using the experimental values T_c [10, 6, 11]. In the Table obtained values of the parameters[1] of the theory and T_c are given for GeTe, PbTe and $Pb_{0.93}Sn_{0.07}Se$.

As it can be seen from the Table, the initial frequencies of FE vibrations for the considered $A^{IV}B^{VI}$ semiconductors are close in magnitude[2] and the relations ω_L/ω_0 are reasonable (*LO* vibration frequencies ω_L for some $A^{IV}B^{VI}$ systems are given in [5]). The values of the obtained frequencies ω_0 are somewhat more than ω_0 ($BaTiO_3$), as determined on the basis of the vibronic theory for $BaTiO_3$ [2], although ω_L ($BaTiO_3$) $>$ $>\omega_L$ ($A^{IV}B^{VI}$). At the same time it is seen that if in simplest vibronic models [13–15] a higher T_c corresponds to the greater value of the constant of the vibronic interaction V, then for $A^{IV}B^{VI}$ semiconductors considered here the situation is reversed. The thing is that the value of T_c is essentially determined by the parameters of electronic spectra. Here a sort of competition takes place between the vibronic contributions to the soft-mode frequency, connected with quasi-one-dimensional (characterized by $\overline{\alpha}_{20}$; $\mathfrak{T}_{\parallel}$) and quasi-two-dimensional ($\overline{\alpha}_{10}$, $\mathfrak{T}_{\perp}$) spectra, respectively. This agrees with the results of [4], where it is shown, for example, that at $\Delta=0$ in the case of quasi-one-dimensional energetic spectra of electronic bands, FPT occurs at a very weak electron-phonon interaction. From the Table it follows that T_c is lowered with the increase of the anisotropy coefficient $k_1=\overline{\alpha}_{10}/\overline{\alpha}_{20}$. The existence of ferroelectric properties below the melting temperature in the $A^{IV}B^{VI}$ semiconductors considered here is essentially connected with the anisotropy of electronic spectra. An analysis shows that the greater part of the vibronic contribution ot the coefficients of the free energy is determined by the region of $E_{1,2}(\mathrm{k})$ spectra near the L-extrema of bands. According to (1.41)—(1.52), the frequency Ω_{hs} strongly depends on the parameters of the anisotropy of electronic spectra $s_{1,2}$. The parameter s_1 is independent of $k_{\parallel 0}$ and s_2 depends weakly on $k_{\parallel 0}$ only in case $\gamma_{10,20} \neq 0$ (at $\gamma_{10,20}=0$,

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[1] Table gives the electronic parameters of $Pb_{0.93}Sn_{0.07}Se$ $\overline{\mathfrak{T}}^2_{\perp,\parallel}$, $\overline{\alpha}_{10,20}$ and $\gamma_{10,20}$ for $s_2(T)$ at $T=T_c$ (in GeTe and PbTe s_2 is independent of T).

[2] The numerical values of $\bar{K}_0/\omega_0$ obtained here are smaller than those used in [12]. At this the temperature T_* of the appearance of the helicoidal structure [12] is lower than T_c and, apparently, such phase in $A^{IV}B^{VI}$ systems is not realized.

$s_1=s_2$). The dependence of Ω_{hs} on $k_{\|0}$ is through $\bar{E}_{1,3}$, but with the increase of $k_{\|0}$ (at the variation of N from 0 up to $2N_0$ in (1.37)) it becomes weak. Therefore, the neglecting of terms containing $G_{1,2,3}$ in (1.5) is justified.

As it is seen from the Table in GeTe, the temperature dependence of the soft-mode frequency Ω_{hs} is provided by the phonon-phonon interactions $\bar{A}$ ($V_0\approx 0$ in accordance with the weak dependence of E_g on T above T_c in GeTe). In PbTe and $Pb_{0.93}Sn_{0.07}Se$ the dependences of Ω_{hs} on T are determined by the dynamical part of the vibronic interaction V_0. To the value of the Curie-Weiss constant $C=6\cdot 10^5$ K measured in $Pb_{0.973}Ge_{0.027}Te$ [16] at $\bar{A}_0=20$ (nm)$^{-2}$ corresponds the effective charge $\bar{e}=3.5e$.

Further, on the basis of (2.1)—(2.14) by using the values of the parameters given in the Table and by taking $\eta_{1,2ph}=0$, $T=0$ we have calculated for GeTe the coefficients of the electron-phonon anharmonicity $\beta_1=101.22$, $\beta_2=50.56$ eV(nm)$^{-4}$. Here condition for the realization of rhombohedral phase (2.21) is fulfilled. The spontaneous lattice distortion $x_0/\sqrt{N_0}$ at $\Delta T=T_c-T\sim 100$ K (at lower temperatures it is necessary to consider the terms $\sim y_i^6$ in (1.11)), calculated by (1.30), is equal to 0.024 nm for GeTe, which agrees quite well with the experimental values of $x_0/\sqrt{N_0}=0.027$ nm obtained at[3] 300 K in [17]. Thus, the electron-phonon interaction joins in itself the driving interaction responsible for the occurrence of the dynamical instability of the paraphase ($\Omega^2_{hs}(T)<0$ at $T<T_c$) as well as the stabilizing interaction restoring the stability of the lattice below T_c in the new equilibrium configuration corresponding to $y_{i0}/\sqrt{N_0}=0$ ($\Omega^2_{z;x,y}>0$ at $T<T_c$), i.e. the electron-phonon interaction is the cause for FPT in $A^{IV}B^{VI}$.

In the systems with the inversion of electronic bands and $\gamma_{10,20}\neq 0$ (as, e.g. in $Pb_{1-x}Sn_xSe$) the temperature dependence of the FE mode frequency according to (1.41) may be nonmonotonic. In particular, with $|\Delta+2E_F+\Delta_1(T)|\sim\dfrac{2\bar{\mathfrak{T}}^2_{\|}}{\bar{\alpha}_{20}}$ the dependence of Ω_{hs} on T can reveal a drop at $T<T_i$ (T_i is the inversion temperature of the bands) in accordance with the experimental dependence of $\Omega_{hs}(T)$ for $Pb_{1-x}Sn_xSe$ [11]. Besides, with $|\Delta(x)+2E_F+\Delta_1|\sim\dfrac{2\bar{\mathfrak{T}}^2_{\|}}{\bar{\alpha}_{20}}$ in the systems $A^{IV}_{1-x}B^{IV}_xC^{VI}$ the change of Δ with x can lead to a nonmonotonic dependence T_c on x, passing through the maximum.

3. Conclusions

For a complete comparison of the theory with the experiment it is necessary to calculate numerically, on the basis of (1.11)—(1.25) for concrete $A^{IV}B^{VI}$ systems, the temperature dependences of elastic constants and the contribution of the spontaneous strains to the ferroelectric characteristics of $A^{IV}B^{VI}$-compounds and to consider the first-order FPT. These results will be published elsewhere.

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[3] At $\Delta T>100$ K $x_0/\sqrt{N_0}$ depends weakly on temperature.

REFERENCES

1. *Консин П. И.* Физ. твердого тела, **24**, вып. 5, 1321—1327 (1982).
2. *Кристофель Н. Н., Консин П. И.* Успехи физ. наук, **120**, вып. 3, 507—510 (1976).
3. *Гиршберг Я. Г., Тамарченко В. И.* Физ. твердого тела, **18**, вып. 11, 3340—3347 (1976).
4. *Konsin, P.* Phys. status solidi (b), **76**, № 2, 487—496 (1976); **86**, № 1, 57—66 (1978).
5. *Dalven, R.* Solid State Phys., **28**, 179—223 (1973).
6. *Kobayashi, K. L. J., Kato, Y., Komatsubara, K. F.* Prog. Crystal Growth Charact., **1**, № 1, 117—149 (1978).
7. *Altukhov, V. I.* Synergetics. Proc. Int. Symp. Synergetics and Cooperative Phenomena in Solids and Macromolecules. Tallinn, «Valgus», 1983, 83—90.
8. *Брандт Н. Б., Белоусова О. Н., Зломанов В. П., Пономарев И. Г., Скипетров Е. П., Штанов В. И.* Ж. эксперим. и теор. физ., **74**, вып. 2, 646—657 (1978).
9. *Kawamura, H., Nishikawa, S., Murase, K.* Proc. Int. Conf. on Appl. High Mag. Field in Semicond. Phys. Oxford, 1978, 170.
10. *Лайнс М., Гласс А.* Сегнетоэлектрики и родственные им материалы. М., «Мир», 1981.
11. *Водопьянов Л. К., Кучеренко И. В., Шотов А. П., Шерм Р.* Письма в ЖЭТФ, **27**, вып. 2, 101—104 (1978).
12. *Шнеерсон В. Л.* Физ. твердого тела, **21**, вып. 11, 3234—3243 (1979).
13. *Берсукер И. Б., Вехтер Б. Г.* Физ. твердого тела, **9**, 2652—2660 (1967).
14. *Консин П. И., Кристофель Н. Н.* Изв. АН ЭССР. Физ. Матем., **18**, № 4, 438—444 (1969).
15. *Дугаев В. К., Литвинов В. И.* Физ. твердого тела. **25**, вып. 1, 136—143 (1983).
16. *Гришечкина С. П., Жоховец С. В., Шотов А. П.* Физ. твердого тела, **22**, вып. 8, 2516—2518 (1980).
17. *Жукова Т. В., Заславский А. И.* Кристаллография, **12**, № 1, 37—39 (1967).

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$A^{IV}B^{VI}$ ÜHENDITES ELEKTRON—FOONON—INTERAKTSIOONI POOLT INDUTSEERITUD SENJETTELEKTRILISTE FAASISIIRETE MIKROSKOOPILINE TEOORIA. 2

On arvutatud vibroonse anharmoonilisuse koefitsiendid, mis stabiliseerib tetragonaalse, rombilise ja romboeedrilise faasi $A^{IV}B^{VI}$ ühendites. Näidatakse, et elektrontsoonide inversiooniga $A^{IV}_{1-x}B^{IV}_{x}C^{VI}$ süsteemides on võimalik mittemonotoonne sõltuvus $T_c(x)$, mis omab maksimumi. On määratud teooria parameetrid ja võrreldud töö 1. ja 2. osas arendatud teooriat eksperimendiga GeTe, PbTe ja $\mathrm{Pb}_{0,93}\mathrm{Sn}_{0,07}\mathrm{Se}$ juhul.

П. КОНСИН

МИКРОСКОПИЧЕСКАЯ ТЕОРИЯ СЕГНЕТОЭЛЕКТРИЧЕСКИХ ФАЗОВЫХ ПЕРЕХОДОВ, ИНДУЦИРОВАННЫХ ЭЛЕКТРОН-ФОНОННЫМ ВЗАИМОДЕЙСТВИЕМ В СОЕДИНЕНИЯХ $A^{IV}B^{VI}$. 2

Рассчитаны коэффициенты электрон-фононной ангармоничности, стабилизирующей тетрагональную, ромбическую и ромбоэдрическую фазы в соединениях $A^{IV}B^{VI}$. Показано, что в системах $A^{IV}_{1-x}B^{IV}_{x}C^{VI}$ с инверсией электронных зон зависимость $T_c(x)$ может быть немонотонной, проходящей через максимум. Определены параметры теории и проведено сравнение развитой в первой и второй частях работы теории с экспериментом для GeTe, PbTe и $\mathrm{Pb}_{0,93}\mathrm{Sn}_{0,07}\mathrm{Se}$.