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FERROELECTRIC PHASE TRANSITIONS INDUCED BY ELECTRON-PHONON INTERACTION IN NARROW-GAP SEMICONDUCTORS

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The theory of ferroelectric phase transitions in narrow-gap semiconductors (PbTe-, GeTe-type systems) has been developed with electron-phonon and phonon-phonon interactions and the degeneracy of active electronic and phonon states taken into account.

The electron-phonon mechanism of structural phase transitions (see, e.g. [1-3]) has been successfully applied to the explanation of some experimental data on narrow-gap ferroelectric-semiconductors (the dependence of the soft mode frequency on temperature, the shift of the Curie point in the magnetic field, etc.) [4-7].

In this report the theory of ferroelectric phase transitions in narrow-gap semiconductors (PbTe-, GeTe-type systems) has been developed with electron-phonon and phonon-phonon interactions taken into account. The real band structure [8,9], the electron-phonon interaction between the valence and conduction bands and the intraband interactions have been taken into consideration.

The initial Hamiltonian is the following:

$$H = \sum_{\sigma,\vec{k}} \varepsilon_\sigma(\vec{k}) a^+_{\sigma\vec{k}} a_{\sigma\vec{k}} + \sum'_{\sigma,\sigma'} \sum_{\vec{k}} P_{\sigma\sigma'}(\vec{k}) a^+_{\sigma\vec{k}} a_{\sigma'\vec{k}} + \frac{1}{2} \sum_{\vec{q},j} (M_j^{-1} P_{\vec{q}j} P_{-\vec{q}j} + M_j \omega^2_{\vec{q}j} y_{\vec{q}j} y_{-\vec{q}j}) + H_{e\text{-}ph} + H_{ph\text{-}ph} . \quad (1)$$

Here $\varepsilon_\sigma(\vec{k})$ are the "initial" electronic spectra of the valence (σ=1,2) and conduction (σ=3,4) bands, respectively, with the wave functions $|L^6_1\alpha\rangle$, $|L^6_2\beta\rangle$ and $|L^6_3\alpha\rangle$, $|L^6_4\beta\rangle$ (α,β are spin indices); $y_{\vec{q}j}$ are normal coordinates, and $P_{\vec{q}j}$ conjugated momenta of active vibrations with the "initial" frequencies $\omega_{\vec{q}j}$ ($\vec{q}$ is the wave vector of phonons; j, the vibrational branch index); M is the reduced mass corresponding to active vibrations. The second term in (1) describes the $\vec{k}\vec{p}$ interaction between the bands. Hamiltonians He-ph and Hph-ph are those of the electron-phonon and phonon-phonon interactions.

We find on the basis of (1) an electronic spectrum, which is renormalized by the electron-phonon interaction:

$$E_{1,2}(\vec{k}) = \frac{1}{2}[\tilde{\varepsilon}_1(\vec{k}) + \tilde{\varepsilon}_2(\vec{k})] \pm \{[\frac{\tilde{\varepsilon}_2(\vec{k}) - \tilde{\varepsilon}_1(\vec{k})}{2}]^2 + P_\perp^2 k_\perp^2 + P_\parallel^2 k_\parallel^2 + V_\parallel^2 z_L^2 + V_\perp^2 (x_L^2 + y_L^2) + 2P_\parallel V_\parallel k_\parallel z_L + 2P_\perp V_\perp [k_x x_L + k_y y_L]\}^{1/2} , \quad (2)$$

where

$$\tilde{\varepsilon}_\sigma(\vec{k}) = \varepsilon^*_\sigma(\vec{k}) + D^\sigma_\perp(\varepsilon_{xx}+\varepsilon_{yy}) + D^\sigma_{\parallel}\varepsilon_{zz} + \beta^\sigma_\perp(x_L^2+y_L^2) + \beta^\sigma_{\parallel} z_L^2 \ , \quad (3)$$

$$\varepsilon^*_{1,2}(\vec{k}) = \varepsilon_{1,3}(\vec{k}) + \varepsilon^{(1,2)}_{dyn} \ ; \ \varepsilon_1(\vec{k})=\varepsilon_2(\vec{k}), \ \varepsilon_3(\vec{k})=\varepsilon_4(\vec{k}) \ ; \quad (4)$$

$$\varepsilon^{(1)}_{dyn} = \sum_{\vec{q}}\left[\frac{V^2_{22}(\vec{q})}{\varepsilon_2(\vec{k})-\varepsilon_2(\vec{k}+\vec{q})+\hbar\omega_{\vec{q}}} - \frac{V^2_{12}(\vec{q})}{\varepsilon_1(\vec{k})-\varepsilon_2(\vec{k}+\vec{q})+\hbar\omega_{\vec{q}}}\right] x$$

$$x \ \frac{\hbar}{M\omega_{\vec{q}}} \ \mathrm{cth}\frac{\hbar\omega_{\vec{q}}}{2k_BT} \ , \quad (5)$$

$$\varepsilon^{(2)}_{dyn} = \sum_{\vec{q}}\left[\frac{V^2_{11}(\vec{q})}{\varepsilon_1(\vec{k})-\varepsilon_1(\vec{k}+\vec{q})+\hbar\omega_{\vec{q}}} - \frac{V^2_{12}(\vec{q})}{\varepsilon_1(\vec{k}+\vec{q})-\varepsilon_2(\vec{k})+\hbar\omega_{\vec{q}}}\right] x$$

$$x \ \frac{\hbar}{M\omega_{\vec{q}}} \ \mathrm{cth}\frac{\hbar\omega_{\vec{q}}}{2k_BT} \ .$$

Here $D^\sigma_\perp$ and $D^\sigma_{\parallel}$ are the constants of deformation potential for acoustical vibrations and the corresponding bands; $V_{\perp,\parallel}$ and $\beta^\sigma_{\perp,\parallel}$ are the constants of the linear interband and quadratic intraband electron-phonon interactions for the ferroelectrical optical mode; $V^2_{\sigma\sigma}(\vec{q}) = \frac{1}{3}(2V^2_{\sigma\sigma\perp}(\vec{q})+V^2_{\sigma\sigma\parallel}(\vec{q}))$ and $V^2_{12}(\vec{q})=\frac{1}{3}(2V^2_\perp(\vec{q})+V^2_{\parallel}(\vec{q}))$; $V_{\sigma\sigma_\perp,\parallel}$ are the constants of the linear intraband interactions; z_L, $x_L \pm iy_L$ and ε^L_{xx}, ε^L_{yy}, ε^L_{zz} are the coordinates of the active optical mode and the components of strains in the system of symmetry axes of L extrema.

On the basis of (1) and (2) the interband electron-phonon interaction is shown to induce the ferroelectric phase transition, if

$$\frac{8}{3M\omega_o^2 N_o}\sum_{\vec{k}}\left[\frac{2V^2_\perp(\vec{k})+V^2_{\parallel}(\vec{k})}{\varepsilon^*_2(\vec{k})-\varepsilon^*_1(\vec{k})}\right] > 1 \ , \quad (6)$$

where N_o is the number of unit cells in a crystal. From (6) it follows that the strong electron-phonon interaction, the small "initial" forbidden gap Δ, the soft "initial" phonon frequency ω_o and the anisotropy of electronic spectra give rise to ferroelectricity in narrow-gap semiconductors.

With the account of strains an expression of the free energy F of GeTe-type ferroelectric-semiconductors has been obtained. At this the terms of all types postulated in the phenomenological theory [10] are generated by the electron-phonon interaction in the expression F. Criteria for the occurrence of coherent lattice distortion (spontaneous polarization) along the axes of types [100], [110] and [111] have been obtained. An essential role in the stabilization of low-symmetry phases is also played by the intraband electron-phonon interaction. The electron-phonon interaction generates the soft optical mode and the temperature dependences of the elastic constants c_{11}, c_{12} and c_{44}, experimentally established in [11].

We also find the forbidden gap, which is renormalized by the electron-phonon interaction in narrow-gap ferroelectric-semicon-

ductors. Going from the components $x_{\perp}$, $y_{\perp}$, $z_{\perp}$ and $\varepsilon_{\alpha\alpha}^{\perp}$ (α=x,y,z) to the corresponding components in the system of the basic axes of a crystal, we obtain on the basis of (2) the forbidden gap for the rhombohedral phase ($x_o=y_o=z_o\neq 0$, $\varepsilon_{xx_o}=\varepsilon_{yy_o}=\varepsilon_{zz_o}\neq 0$, $\varepsilon_{xy_o}=\varepsilon_{yz_o}=\varepsilon_{zx_o}\neq 0$) :

$$E_{g1}(T) = 2\{[\tfrac{1}{2}(\Delta+\varepsilon^{(1)}_{dyn}(T)-\varepsilon^{(2)}_{dyn}(T)) + 3[\Lambda^{-}\varepsilon_{xx_o}+\Lambda_1^{-}\varepsilon_{xy_o}+ +(\beta^{-}+\beta_1^{-})x_o^2]]^2 + 3(K_o+K_1)x_o^2\}^{\frac{1}{2}}, \tag{7}$$

and

$$E_{g2}(T) = 2\{[\tfrac{1}{2}(\Delta+\varepsilon^{(1)}_{dyn}(T)-\varepsilon^{(2)}_{dyn}(T)) + 3[\Lambda^{-}\varepsilon_{xx_o} - \tfrac{1}{3}\Lambda_1^{-}\varepsilon_{xy_o}+ +(\beta^{-}-\tfrac{1}{3}\beta_1^{-})x_o^2]]^2 + 3(K_o-K_1)x_o^2\}^{\frac{1}{2}}, \tag{8}$$

where $K_o=\frac{1}{3}(2V_{\perp}^2+V_{\parallel}^2)$, $K_1=\frac{2}{3}(V_{\parallel}^2-V_{\perp}^2)$ and

$$A^{-} = \tfrac{1}{2}[A_{\perp}^{-} + \tfrac{1}{3}(A_{\parallel}^{-}-A_{\perp}^{-})],$$

$$A_1^{-} = \tfrac{1}{3}[A_{\parallel}^{-}-A_{\perp}^{-}],\quad A_{\perp,\parallel}^{-} = A_{\perp,\parallel}^{(1)} - A_{\perp,\parallel}^{(2)}$$

with $A\equiv\Lambda,\beta$. The minimum gap may be E_{g1} or E_{g2}, depending on the actual values of the constants of electron-phonon interaction. At $T>T_c$ $\frac{dE_g}{dT}>0$, if the contribution from the interband electron-phonon interaction in $\varepsilon^{(1,2)}_{dyn}$ exceeds that from the intraband electron-phonon interaction. For many PbTe-type systems $\frac{dE_g}{dT}>0$ at $T>T_c$. We show that in GeTe the forbidden gap E_{g1} is the minimum one and E_{g1} as a function of temperature has its minimum below T_c in accordance with the experiment [12].

References

1) P. Konsin: phys. stat. sol. (b) 76 (1976) 487.
2) P. Konsin: phys. stat. sol. (b) 86 (1978) 57.
3) N. Kristoffel, P. Konsin: Ferroelectrics 6 (1973) 3.
4) H. Kawamura, K. Murase, S. Nishikawa, S. Nishi, S. Katayama: Solid State Commun. 17 (1976) 341.
5) P. Konsin, N. Kristoffel: Proc. Int. Conf. Phys. Semicond. (1978) 453.
6) A. Benyon, A.D.C. Grassie: J. Vacuum Sci. Technol. 10 (1973) 678.
7) K. Murase, S. Sugai, S. Takaoka, S. Katayama: Proc. Int. Conf. Phys. Semicond. (1976).
8) J.D. Dimmock: The Physics of Semimetal and Narrow-Gap Semiconductors p.319 (1970).
9) G. Martinez: Phys. Rev. 8 (1973) 4678.
10) A.F. Devonshire; Phil. Mag. 40 (1949) 1040; J.C. Slonczewski, H. Thomas: Phys. Rev. B1 (1970) 3599.
11) S. Sugai, K. Murase, T. Tsuchihira, H. Kawamura: Phys. Soc. Japan 47 (1979) 539.
12) P.J. Stiles, L. Esaki, W.E. Howard: Proc. Int. Conf. Low Temp. Physics (1967).