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FERROELECTRIC PHASE TRANSITION IN IV-VI SEMICONDUCTORS

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IV-VI semiconducting compounds such as PbS, PbSe, PbTe and SnTe exhibit a strong soft-mode behavior which is attributed to a ferroelectric phase transition. Within a non-linear chain model the transverse acoustic (TA) and the ferroelectric transverse optic (TO) mode have been calculated for these compounds and compared to experimental data. The results are interpreted in terms of a three-dimensional model and are compared to the electronic band structure.

I. Introduction

Recently [1] the dynamical properties of ferroelectric perovskites have been successfully described in terms of a strongly anisotropic quartic polarizability of the oxygen ion. The essential features of the model could be reproduced in a simplified version [2] by a diatomic linear chain treatment with non-linear temperature dependent polarizability at the chalcogenide sublattice site. Within this model the TA and the ferroelectric TO modes have been calculated for PbS, PbSe, PbTe and SnTe, and good agreement with experimental data has been achieved.

II. The Model

The "pathological" behavior of O^{2-} and its homologues [3][4] has been taken into account within a linear diatomic shell model (Fig. 1), which consists of a highly polarizable anion (m_1) and the weakly polarizable cation (m_2). The instability of the ferroelectric mode is attributed to a negative electron-ion coupling constant g_2, which takes into account strongly attractive Coulomb forces. Above the phase transition the paraelectric modes are stabilized by the repulsive onsite fourth-order core-shell coupling g_4 and the second-nearest neighbor core-core coupling constants f' and f". This is sufficient to guarantee the stability of the lattice in the ferroelectric phase. The harmonic core-shell coupling h at the cations has small but non-negligible values. With periodic boundary conditions the model yields the following dispersion relations in the adiabatic approximation:

$$\omega_{\pm}^2 = \tilde{f}\{\frac{1}{m_1}((\frac{2f}{h} + \frac{4f'}{\tilde{f}})\sin^2 qa + 1) + \frac{1}{m_2}((\frac{2f}{g} + \frac{4f''}{\tilde{f}})\sin^2 qa + 1)\} \pm$$
$$\tilde{f}\{(\frac{1}{m_1}((\frac{2f}{h} + \frac{4f'}{\tilde{f}})\sin^2 qa + 1) - \frac{1}{m_2}((\frac{2f}{g} + \frac{4f''}{\tilde{f}})\sin^2 qa + 1))+\frac{4\cos^2 qa}{m_1 m_2}\}^{\frac{1}{2}}$$

where $\tilde{f} = \dfrac{fgh}{(2f + g)(2f + h) - 4f^2\cos^2 qa}$

At q=0 the ferroelectric TO mode is given by: $\omega_f^2(q=0) = \dfrac{2\tilde{f}}{\mu} = \omega_0^2 \cdot \dfrac{\tilde{f}}{f}$

The temperature dependence of ω_f is mainly determined by $g = g_2 + 3g_4\langle w^2\rangle$, where in the self-consistent phonon approximation (SPA) the non-linear term $g_4\langle w^3\rangle$ is replaced by a linearized term [2] . Four different temperature regimes [5] for ω_f are to be distinguished: the quantum limit for $T_c \simeq 0$ where $\omega_f^2 \approx T^2$ [6] , the dimensionality-crossover region [7] $\omega_f^2 \approx (T-T_c)^\gamma$, $\gamma = 1.4-1.6$, the mean-field regime for $T > T_c < T_f$ and at high-enough temperatures, a regime with saturation ($\gamma = 1/3$).

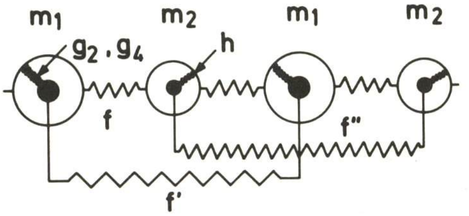

Fig. 1 The model

III. Results

Within this model the dispersion curves for the TA and the ferroelectric TO mode have been calculated. The model parameters g,h, f,f', f" have been determined by optimizing the fit to the experimental curves. (Fig. 2-5). All these compounds have the cubic NaCl-structure in the paraelectric phase. For the perovskites the pseudo-one dimensional model works well in the (100)-direction [5] for IV-VI compounds the (111)-direction is the equivalent diagonal direction. Starting with the parameter set of PbS the substitution of sulfur by another chalcogenide ion affects mainly the TO mode, which is lowered to smaller values. A slight tuning of the model parameters leads to the calculated curve. The parameters are listed in Tab. 1 for the four crystals. The main changes occur for the nearest neighbor constant f, which increases with increasing overlap between anion and cation. In the same way the anionic polarizability g increases with increasing difference in masses. As g contains the temperature dependence of the soft mode the decrease in g when going from PbS to SnTe indicates the "softness" of the system, which has also been verified experimentally. PbS (largest g) exhibits only a very small temperature dependence for the q=0 TO-mode, while SnTe (smallest g) becomes a real ferroelectric [9]. Our model gives a very transparent physical description of the ferroelectric soft mode behavior in the (111)-direction. For the description of the phonon dispersion curves in a general direction a full shell model including long-range Couloub effects has to be used [10]. In the (111)-direction this model is, to a good approximation, equivalent to our linear chain model. The shell model equations read:

Tab. 1

	PbS	PbSe	PbTe	SnTe
f'	1.65	0.55	0.75	0.98
f"	-1.0	-2.0	-1.8	-2.2
g	0.95	0.85	0.45	0.3
h	28	28	28	28
f	4,5	12	13	18.5

The force constants are given in units of 10^4 dyn/cm

$$M\omega^2 U = \{ R + ZCZ - (T+ZCY)(S+K+YCY)^{-1}(T^+ + YCZ) \} U$$

R,T,S,ZCZ, ZCY and YCY are the coupling matrices specifying the ion-ion, ion-shell and shell-shell short range and long range interaction respectively. The alternating sequence of cations and anions in

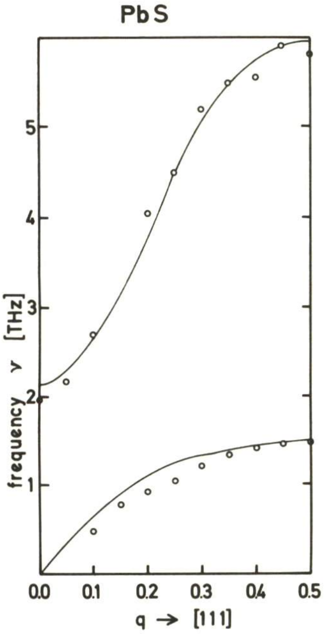

Fig.2 296K [8]

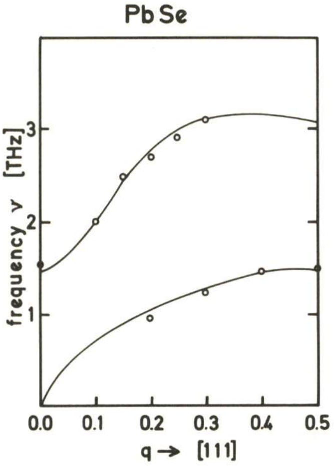

Fig.3 296K [8]

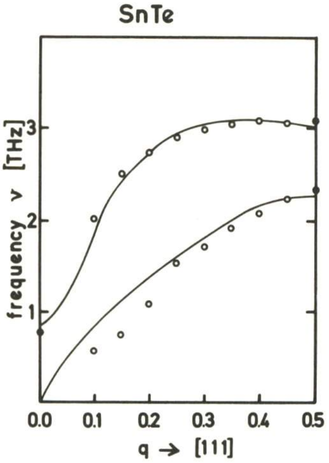

Fig.4 100K [8]

the (111)-direction reduces the Coulomb interaction ZCZ to an effective nearest neighbor force constant. This enhances the longitudinal coupling and decreases the transverse coupling constants. In the shell-core coupling part we have to consider the local-field correction by a renormalization of the shell-core coupling constants g and h. The parameters derived from the shell model of Cochran et al. [10] are compared to the linear-chain parameters in Tab.2.

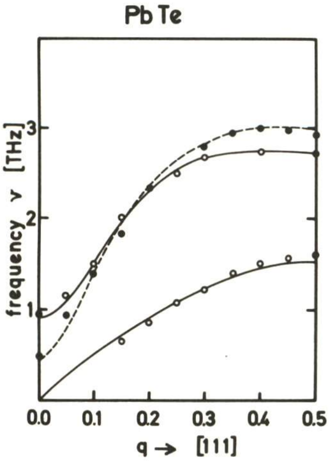

Fig.5 dashed line-4.2K, full line-296K [8]

Tab. 2

f	24.56	11.34	13
f'	-0.13	.13	0.75
f"	-1.17	-1.17	-1.8
h	31.58	34.53	28
g	6.85	0.30	0.45
y_1	-0.799	--	--
y_2	-3.703	--	--
z	-2.15	--	--

The force constants of PbTe are given in units of 10^4 dyn/cm

Column 1: force constants of Cochran for the transverse coupling
Column 2: renormalized force-constants
Column 3: force constants of linear chain-model.

IV. Electronic band structure

It has been shown that the dynamic behavior of the ferroelectric IV-VI compounds can be described in a five-parameter model with three effective short-range and two deformability parameters. The parameters can be compared with those of other ferroelectric compounds in terms of the electronic band structure. The most important quantity of the model is a temperature-dependent deformability of the crystal which may be defined in the limit $h \gg g(T)$ in analogy to the dielectric constant by

$$d(T) = \omega_{TO}^{2}(T) \; / \; \omega_{o}^{2} = 1 + 2f/g(T),$$

$g(T)$ has (similar to the Penn model) the meaning of an effective band gap. For PbTe we obtain from $g(300\ K) = 0.45 \times 10^{4}$ dyn/cm and $g(4.2K) = 0.10 \times 10^{4}$ dyn/cm a fictitious transition temperature T_c of -120 K. In the average band-gap model of Murase [11] this corresponds to $E_g^o = 2$eV at T_c and leads at T = 300 K to an effective gap $E_g^{eff}(300) = E_g(300\ K) - E_g(T_c)$ of 0.45 eV. This value is only 0.11 eV above the measured value [12]of the minimum gap at L and indicates that our model gap parameter $g(T)$ is closely related to the temperature dependent value of the minimum gap.

In the IV-VI semiconductors like in other ferroelectrics the non-linear polarizability is mainly due to the unbound p-electrons in the valence band. There are two contributions to the polarizability, which is determined by $g(T)$:

1) The local field corrections which are strongly enhanced in highly anisotropic systems and play therefore an important role in perovskites while they are of minor importance in IV-VI-compounds.
2) The inverse width of the band gap which is the leading term for the IV-VI-semiconductors and yields extremely large values for the polarizability via the small gap.

It has been shown, that ferroelectric soft modes can be described in terms of a non-linear, quartic, polarizability of the chalcogenide ion. This model gives a unique picture of ferroelectricity in structural completely different compounds. It is interesting to note that via the exact solutions of the non-linear equations of the model domain walls as well as electrooptic phenomena can be understood in terms of solitary excitations [13].

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