PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 725–732

THE STRUCTURAL PHASE TRANSITION IN IV-VI SEMICONDUCTORS

Kazuo Murase

Department of Physics
Osaka University
1-1 Machikane-yama
Toyonaka, 560
Japan

It is discussed that the local movement of the off-center Ge^{2+} ions strongly enhances the transition temperature T_c in $Pb_{1-x}Ge_xTe$. The measured dielectric constant is analyzed by the present model. The resistivity anomaly near T_c is studied at stresses along <100>, <110> and <111> crystalline directions. We also investigated the band edge structure in the low temperature phase. We found a novel phase transition in the layered semiconductors of the GeSe-SnSe system.

I. Introduction

Among IV-VI compound crystals, lead chalcogenides(PbTe, PbSe, PbS), SnTe, GeTe and their alloys are well known narrow gap semiconductors which are very useful and important materials for infrared lasers and detectors with tunable wavelengths by temperatures[1]. We will now focus our attention on another aspect, namely the lattice instability, of these materials including a group of GeSe, SnSe, SnS and GeS which has an orthorhombic structure in contrast with a NaCl type or a rhombohedral structure of the former. (Pb,Sn,Ge)Te crystals take either a NaCl or a ferroelectric rhombohedral type structure at the absolute zero depending upon alloy compositions. With increasing temperature, a distorted crystal transforms to a NaCl one at a second order or nearly second order transition temperature T_c. The ferroelectric structural phase transition problem has a long history since a suggestion of a large static dielectric constant ε_s in PbTe[2] and succeeding measurements of ε_s in an abrupt junction diode capacitance[3], and by magnetoplasma excitation spectra[4] which were consistent with the discovery of the soft TO modes at the Γ point[5]. The stability of group V elemental crystal structure (As) and IV-VI compound (GeTe) was discussed with a pseudopotential method, where it was pointed out that the relative f.c.c. sublattice displacement $\vec{u}$ is predominantly important and the rhombohedral distortion ε_{ij} is a secondary effect [6]. Following this, the displacement along a <111> direction was measured[7]. Many band structure calculations have been made in average V crystals[8-10]. A new attention was directed to the lattice instability in (Pb,Sn,Ge)Te, since a detailed study of temperature dependent capacitance measurement was made for graded junction diodes [11]. The mechanism of the phase transition has been investigated by means of resistivity anomaly, dielectric constant measurements, ultrasonic propagations, Raman scattering and optical dielectric constant ε_∞ anomaly as well as x-ray and neutron diffractions[12]. An importance of interband electron-TO phonon interactions[13-15] was claimed in the PbTe-SnTe system where the minimum energy gap becomes zero at a certain composition and temperature[13]. It was revealed, however,

that the zero gap effect on the lattice instability is very small due to the small density of states at the band edge[16]. The renormalized TO phonon frequency is decomposed as

$$\omega_{TO}^2 = \omega_o^2 + \omega_A^2(T) - \Delta\omega^2 \quad , \tag{1}$$

where $-\Delta\omega^2$ is due to the interband electron-TO phonon interactions, ω_o^2 a certain positive term. The temperature dependence of ω_{TO}^2 mainly comes from the phonon-phonon interaction term $\omega_A^2(T)$. The transition temperature may be determined by $\omega_{TO}^2=0$ in eq. (1). The physical quantities are gradually changed with composition x in $Pb_{1-x}Sn_xTe$, where the deviation from the stoichiometry increases up to ~1%. The free carriers are supplied by the defects due to the deviation. Apparent carrier concentration dependences of ω_{TO}^2 and T_c have been interpreted by the electron-TO phonon interaction mechanism [17]. The effects of defects may not be, however, overlooked in the lattice instability[18]. In $Pb_{1-x}Ge_xTe$, the transition temperature rapidly increases with increasing Ge content x [19]. The resistivity anomaly cannot be fully analyzed by a carrier-soft phonon scattering mechanism[20,21] as attempted in SnTe[22]. The fact that the minimum band gap increases with x in $Pb_{1-x}Ge_xTe$[23] suggests us that the lattice instability is essentially determined by excitations over an average gap or a bond gap[23,24], since the larger minimum gap would lower the transition temperature by the interband contribution $-\Delta\omega^2$ near the band edge. A 'bonds and bands' picture such as a spectroscopic approach is successful in understanding the crystal stability in <V> crystals[25-27]. The large transverse effective charge has been interpreted[27-29]. The (Ge,Sn)-(Se,S) system forms apparently quite different universe from lead chalcogenides, SnTe, GeTe and their alloys which has about 1 eV minimum gap[30].

In this paper, we will report our recent investigations of the mechanism of the phase transition in the PbTe-GeTe system where we direct our attention to an important role of Ge ions in the lattice instability and effects of crystal distortions on T_c and the band structure below T_c. The newly observed anomalies in resistivity and Raman works in the GeSe-SnSe system will be briefly presented.

II. Phase Transition in $Pb_{1-x}Ge_xTe$

1. A Role of Ge Ions on Structural Instability

A number of apparently different features have been observed about the phase transition in $Pb_{1-x}Ge_xTe$[19-21] in comparison with $Pb_{1-x}Sn_xTe$. The transition temperature drastically increases from zero to 220K with increasing x up to 0.1. Moreover the temperature dependence of the inverse static dielectric constant $1/\varepsilon_s$ shows a significantly different behavior from that of $Pb_{1-x}Sn_xTe$[31]. The electrical resistivity anomaly cannot be fully explained by a simple theory with the scattering of carriers from the soft TO phonons[20,21] which reasonably reproduced the anomalous increment $\Delta\rho$ of the resistivity near T_c in SnTe. These effects positively suggest an importance of the role of germanium atoms in the alloy[32]. The Ge ions may be unstable to the displacement from the substitutional cation sites, because of the small ionic radius of Ge^{2+}(0.73Å) compared with that of the Pb^{2+} ions(1.2Å). The local dipole arises from the displacement. We imagine that the dipoles due to the off-center Ge ions interact with each other through the lattice polarization field(optical phonons) of a modified PbTe medium as well as via the pure dipole-dipole coupling. At low temperatures the dipoles may be put in order promoted by the softening of the TO phonons in the medium. Conversely,

an instability of the medium NaCl type lattice comes to be enhanced by the dipoles. There may appear eight equivalent off-center positions along <lll> directions. For simplicity the present system may be reduced to the coupled system of the pseudospin with the optical phonons assuming the dynamics of the Ge ion in a two-well potential along a particular <lll> direction parallel to the relative displacement of sublattices. The germanium ion may transfer from one well to the other by interactions between its local dipole and the lattice polarization through the local field. The tunneling mechanism may not be precluded for the transfer.

The phase transition temperature T_c is determined by the equation:

$$1 = (G/\tilde{E}_o)\tanh(\tilde{E}_o/k_B T_c) \quad , \tag{2}$$

instead of eq. (1), where G is a parameter of the dipole-dipole interactions determined by the lattice polarizability and the local dipoles; $\tilde{E}_o$ the renormalized transfer energy between wells. The solid line in Fig.(1) is the calculated phase transition temperature. The squared TO phonon frequency ω_{TO}^2 (x,T) in the medium included in G is assumed to be expressed as

$$\omega_{TO}^2 = \alpha\{T_1 \coth(T_1/T) - T_c^o(x)\} \quad , \tag{3}$$

with

$$T_c^o = (1-x)T_c^{PbTe} + xT_c^{GeTe} \quad . \tag{4}$$

The value T_c^{PbTe}=-77.5K is a typical Curie temperature of PbTe[11,30], and T_c^{GeTe} is chosen to be the phase transition temperature 670K in GeTe[19]. Parameters, α and T_1, were obtained to reproduce $(1/\varepsilon_s)$ of PbTe in Fig.(2): $\alpha=1.02\times10^{23}(\text{rad/sec})^2\text{K}^{-1}$ and $T_1=37.8\text{K}(\sim T_D/4)$. The relative magnitude η of the pure and phonon mediated dipole-dipole interactions is chosen to be 0.345 to adjust the calculated T_c with the experimental data at x=0.01 and 0.1. At $\tilde{E}_o$=1K, the composition x_c, x at T_c=0, is 0.00026. In order to fit x_c with the observed value x_c=0.005 as shown in the broken line below x=0.01, $\tilde{E}_o$ must be taken to be 19.3K which seems to be an unrealistically large value. There may be additional or alternative mechanisms such as a percolation

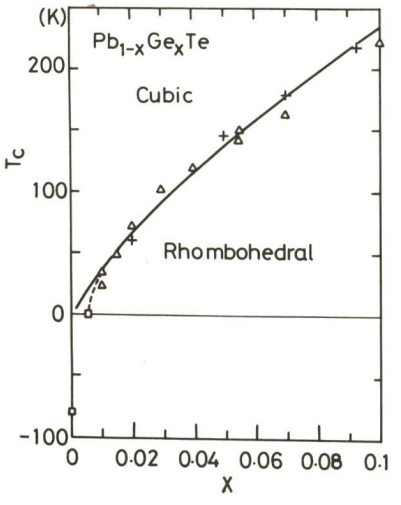

Fig. 1 T_c vs x in $Pb_{1-x}Ge_xTe$; the transition temperature(△) by resistivity anomaly[20,21], (+) x-ray[19] and (□) by a magnetoplasma experiment[31]

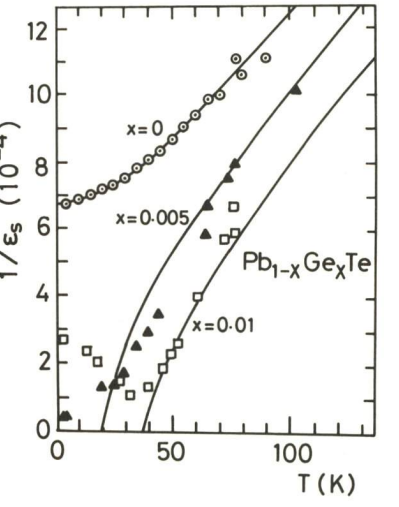

Fig. 2 Inverse dielectric constant at 50GHz. The solid line follows calculations $1/\varepsilon_s(0)$ in the text

effect to understand the strong deviation of T_c from our mean field values in the dilute region.

The dielectric function above T_c was derived by evaluating the dipole-dipole correlation functions in a mean field scheme[32]. The dielectric function is apparently expressed as a sum of the lattice and the local term due to the collective motion of Ge^{2+} ions. In the static limit ($\omega \to 0$), the function is given as

$$1/\varepsilon_s(0) \simeq (1/\varepsilon_s)\{1 - (G/\tilde{E}_o)\tanh(\tilde{E}_o/k_BT)\} \quad , \tag{5}$$

and $$\sim(1/\varepsilon_s)(1 - T_c/T), \qquad \text{for } \tilde{E}_o < k_BT_c \quad , \tag{6}$$

where $1/\varepsilon_s$ is the static dielectric constant due to phonons. The inverse dielectric constant was measured by means of mm-wave magneto-plasma reflection as shown in Fig.(2). The solid curve shows the calculated value. For PbTe the curve has been fitted with data with a Debye model (T_D=150K) [31] which is similar to eq. (3) by an Einstein model. The calculated curve reasonably predicts $1/\varepsilon_s(0)$ for the data at x=0.005 and 0.01 above T_c. Below T_c, we need more detailed analysis.

2. Effect of External Fields

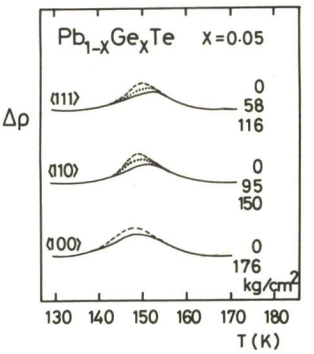

Fig. 3 Increment of resistivity $\Delta\rho$ near T_c for different stresses: The ordinate is of an arbitrary scale. The difference of peak position at zero stress(broken lines) are due to a small difference of $x \sim 0.05$ in specimens

We studied the resistivity anomaly in $Pb_{1-x}Ge_xTe$($x=0.035 \sim 0.05$) near the transition temperature T_c at stresses up to 500kg/cm^2 along <100>, <110> and <111> crystalline directions with currents parallel to the stresses. A peak shift with a simultaneous reduction of the anomaly was observed at uniaxial stresses as shown in Fig.(3). The peak shifts linearly with stresses, the slope of which increases in sequence as <100>, <110> and <111> directions. These are related with the complete softening of the TO phonon modes whose polarizations are perpendicular to the stresses. The anisotropic TO phonon frequencies and order parameters were calculated in the framework of the Landau free energy expansion[33] at stresses along the particular crystalline directions. The reduction of $\Delta\rho$ may be ascribed to the appearance of incomplete soft TO phonons with polarizations not in the perpendicular plane. The experimental stress dependence of T_c in different stress directions, however, could not be fully predicted by the calculation with up to fourth order terms of macroscopic coordinates; shift of T_c per 100kg/cm^2 was estimated as, 0.5, 1.1 and 1.8 by the experiment; -0.2, 1.3 and 0.8 by the calculations for <100>, <110> and <111> stress directions; and -2.0(calculation) for hydrostatic pressures. There should be the relation $3\Delta T_c(111)=\Delta T_c(001)+2\Delta T_c(110)$, but the experimental data do not obey it. The discrepancy might be ascribed to the critical fluctuation and/or an effect of sixth order terms. In fact we confirmed an importance of the sixth order terms in the bias dependent capacitance of the graded p-n junction with (100), (110) and (111) surfaces in $Pb_{1-x}Ge_xTe$. In addition, we found that the capacitance anomaly shows distinct twin peaks for the (111) plane junction at 100 kHz,

which may be associated with the critical slowing down of the local dipoles in section 1. The critical behavior of the elastic constants is apparent in the ultrasonic measurements[33].

3. Distorted Fermi Surfaces below T_c

Below T_c, the static relative displacement $\vec{u}$ of sublattices along a <111> direction grows with the simultaneous rhombohedral shear ($\varepsilon_{ij}=\varepsilon_s$, $i\neq j$) and dilational strains ($\varepsilon_{ij}=\varepsilon_d$, $i=j$). The band edge structure is modified by the distortions. The four equivalent valleys at L-points in a NaCl structure should split into a couple of singlet (s) and triplet (t) valleys with a lift of the Kramers degeneracy due to the broken inversion symmetry of the crystal except for just on the T and L points. The Fermi surfaces are distorted from ellipsoids of revolution and the carrier redistribution occurs among these nonequivalent valleys. We calculated the modified band edge structure taking into account the optical deformation potential term $\Xi u=(\mathrm{grad}_{\vec{u}}V)\cdot\vec{u}$ as well as the strain terms with a six band model, using the wave-functions by Mitchell and Wallis[34].

There are two possible origins for the increment of minimum gap E_g below T_c which was observed in the optical experiments for specimens ($x=0.015\sim0.07$) [23]. One is $\delta E_g(\varepsilon_{ij})$ due to the strains ε_{ij} whose deformation potentials are not available in $Pb_{1-x}Ge_xTe$, but we may use the corresponding ones in PbTe where the shear deformation potentials are positive both for conduction and valence bands. The other is $\delta E_g(\vec{u},\vec{k}_{ex})$ from the relative displacement $\vec{u}$ which generally shifts the band extrema $\vec{k}_{ex}$ from the L and T points. The remote band parameters act importantly on $\delta E_g(\vec{u},\vec{k}_{ex})$. We estimated the value Ξu, as, 0.05, 0.10, 0.12 and 0.17 for specimens with x=1.5, 3.0, 5.5 and 7.0,

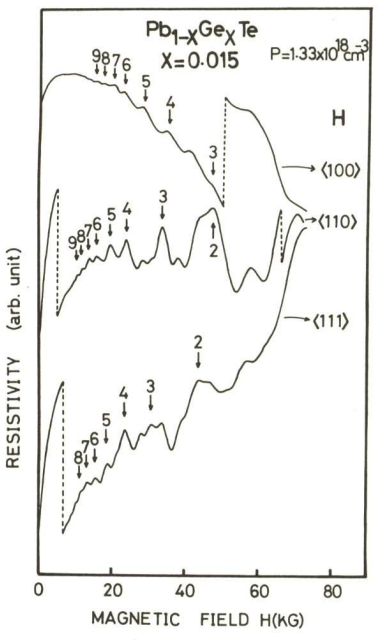

Fig. 4 SdH oscillations below T_c for H// <100>, <110> and <111>

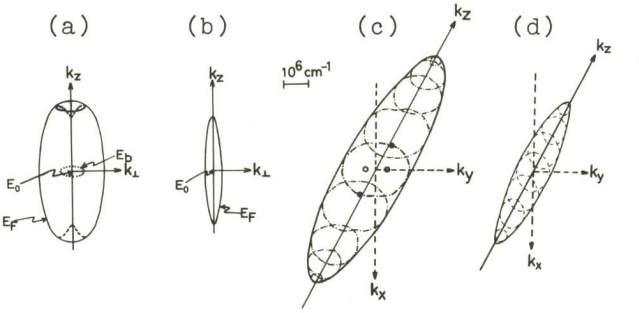

Fig. 5 Fermi surfaces below T_c in $Pb_{1-x}Ge_xTe$($x=0.015$, $n=5.4\times10^{17}cm^{-3}$); (a) larger surface at the s-valley with carrier density $\sim0.88\times10^{17}cm^{-3}$, $E_o=6.2$meV, $E_b=2.9$meV(band minimum along the dotted line) $K\sim4$ and $E_F=12$meV. Two hollows are seen at the top and bottom of the surface. (b) the smaller at the s-valley; with carrier density $0.4\times10^{16}cm^{-3}$, $E_o=6.2$meV (minimum), $K\sim33$ and $E_F=12$meV. (c) the larger surfaces in the t-valley; with carrier density $1.23\times10^{17}cm^{-3}$ $K=11\sim16$ and $E_F=16$meV, $E_o=3.5$meV, (○)1.6meV, (●)1.4meV(minimum). (d) the smaller surfaces in the t-valley; with carrier density $0.22\times10^{17}cm^{-3}$, $E_o=3.5$meV(minimum), $E_F=16$meV and $K=8\sim11$

respectively, by analyzing the increment of the optical energy gap ΔE_g below T_c in such a way as putting $\delta E_g^t(\vec{u})=\Delta E_g - \delta E_g^t(\varepsilon_{ij})$ for the triplet valley, since $\delta E_g^t(\vec{u})$ is smaller than $\delta E_g^s(\vec{u})$.

The Fermi surfaces at the low temperature phase were investigated by the Shubnikov-de Haas (SdH) effect at 4.2K in high mobility and homogeneous single crystals with relatively low $T_c(=30 \sim 50K)$. There appeared 'knotty' oscillations both in n and p type $Pb_{1-x}Ge_xTe$ (x= 0.0125 and 0.015). Figure (4) shows the typical SdH signal, where a background transverse resistance is properly subtracted. There seems to be more than one SdH series even in H// <100> due to the lattice distortions which may indicate the modification of the band edge structure. It should be emphasized that the lift of the Kramers degeneracy due to $\vec{u}$ makes two kinds of the Fermi surfaces in the s- and t-valleys. The prominent oscillations were assigned to larger Fermi surfaces at t-valleys both in n- and p-type specimens. The carrier concentration of the valley N'(or P') was obtained with an assumption that the Fermi surface is still an ellipsoid of revolution with a mass anisotropy factor $K \sim 10$. The parameter Ξu was again estimated, as 0.03 and 0.04 for specimens, x=0.0125(n), and 0.015(n & p), respectively, with the total carrier concentrations by the Hall measurement, using the analytic form of the band edge structure. Our experimental six band parameters[35] were used for the calculation of Fermi surfaces below T_c which are exhibited in Fig.(5) for the specimen(x=0.015, $n=5.4 \times 10^{17}cm^{-3}$). Since the deformation is small in our specimens with the low Ge compositions, the Fermi surfaces of the down-state in the triplet valleys may be approximately regarded as an ellipsoid. The mass anisotropy is expected to be $K=11 \sim 16$. While the large volume s-valley surface is surprisingly distorted and the small s-surface has a strong mass anisotropy $K \sim 33$. These features are consistent with the identification of the prominent SdH frequency, since the down state in the t-valleys has a smaller distortion from the ellipsoid of revolution, and a larger volume. The cyclotron mass m_c^* was calculated for the t-valleys each of which increases by ∿30% at 4.2K compared with the value at T_c. Such phenomena were observed by far-infrared magneto-reflection spectra, where the several magnetic quantum transitions appeared due to a modification near band edges [35]. With increasing x, the Fermi surfaces are tremendously deformed with caves. From the above Ξu values, the optical deformation potential Ξ is estimated to be $15 \sim 20$ eV using an estimation of u^2 [33]. The value is comparable with 21eV by the resistivity anomaly [20] and $20 \sim 48$ eV by shifts of T_c with magnetic fields[21].

III. A Phase Transition in the GeSe-SnSe System

Anomalous behaviors in low temperature resistivities and Raman spectra have been investigated in p-type GeSe and SnSe, each of which has been known to be an orthorhombic structure with double-layer planes(D_{2h}^{16}) at room temperature[36]. In GeSe, a resistivity hump appears ranging between 100 and 200 K with a peak at near 160K as shown in Fig.(7). The resistivity shows hysteresis in the range between 100 and 200 K under a slow temperature-sweep. The anomaly is mainly due to free carrier density change. The room temperature carrier densities are of the order of $10^{17}cm^{-3}$ or less. The Hall mobility assumes near $T^{-1.5}$ law at $T \sim 180K$ and the temperature dependence becomes less steep below 150K such as T^{-1}. It seems that a phase transition occurs near at 185K. The resistivity anomaly is more distinct for a good specimen with higher room temperature carrier concentrations.

New Raman lines typically in the A_g mode configuration grow weakly at 89, 202 and strongly at $228\,cm^{-1}$ at low temperatures accompanied by enhancement of the layer breathing mode ($180cm^{-1}$) intensity as given

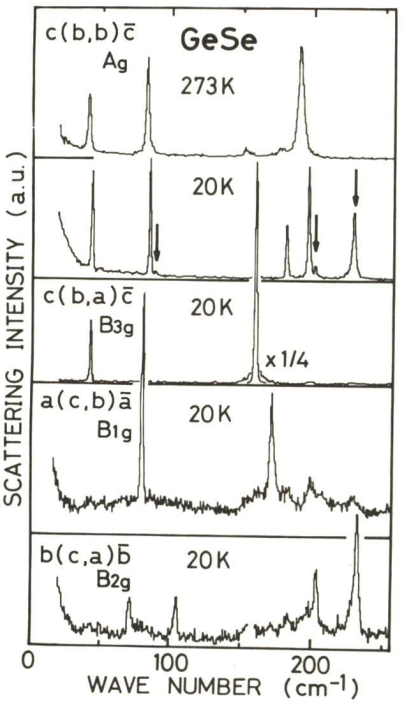

Fig. 6 Raman spectra in GeSe

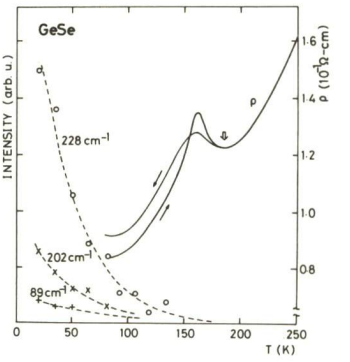

Fig. 7 Resistivity anomaly and growth of new Raman lines in GeSe

in Fig.(6). The peak intensity of the new lines are plotted as functions of temperature in Fig.(7). These facts positively suggest the existence of a new type of phase transition as conjectured. Comparing new peaks with infrared-active modes[37] which have been measured at room temperature, they are closely related to the LO-phonons in B_{3u} configuration (E// c). We infer that the transition may be due to a broken-inversion-symmetry between the double layers; such as $D_{2h} \rightarrow C_{2v}$ due to a small relative displacement of the layers. At present soft modes were not observed both in Raman and infrared spectra. There are also indications of a transition in SnSe below 50K. The carrier density change due to the phase transition in GeSe might be attributed to a carrier localization along domain boundaries. The Raman spectra are rather insensitive to the room temperature carrier concentrations. A change of mobility slope below the transition temperature suggests a modification of the band edge structure. The anomaly near the absorption edge[30] may be due to the band edge transformation.

We presented various experimental works about lattice instabilities in IV-VI compound semiconductors which might help to realize the present situation of the topics, though there remain much discussions and unmentioned works by others as well as by us.

Aknowledgements

The author wishes to thank several peoples in his laboratory for their contributions and many valuable discussions: to Dr. S.Katayama in the theory of structural instability, to Dr. S. Nishi in measurements of dielectric constant, to Dr. S. Sugai, R. Kawabata and K. Matsumoto in the phase transition under external fields, to Dr. S. Takaoka and Dr. S. Nishikawa in the investigation of the band edge structures in $Pb_{1-x}Ge_xTe$; and, to T. Fukunaga, T. Kinosada, Dr. S. Sugai and Dr. S. Ishida in the experiment of the GeSe-SnSe system. He wishes to express his gratitude for the continual interest and encouragement recieved from Prof. H. Kawamura and Prof. J. Kanamori. The work was supported in part by the Kurata Foundation and by the Grant-in-aid for Scientific Research from the Ministry of Education.

References

1) I. Melngailis and T.C. Harman: Semiconductors and Semimetals (Academic Press, New York, 1970) p. 111.
2) E. Burstein and P.H. Egli: Advances in Electronics and Electron Physics, 7 (1955) 56.
3) Y. Kanai and K. Shohno: J. Appl. Phys. 2 (1963) 6.
4) Y. Sawada, E. Burstein, D.L. Carter and L. Testardi: Plasma Effects in Solids (Donod, Paris, 1964) p.71.
5) W. Cochran: Phys. Lett. 13 (1964) 193.
6) M.H. Cohen, L.M. Falicov and Stuart Golin: IBM J. July (1964) 215.
7) J. Goldak and C.B. Barrett: J. Chem. Phys. 44 (1966) 3323.
8) R. Dalven: Solid State Phys. 28 (1973) 179.
9) G. Martinez, M. Schlüter and M.L. Cohen: Phys. Rev. 11 (1975) 651.
10) M. Schlüter, G. Martinetz and M.L. Cohen: Phys. Rev. B11 (1975)3808.
11) R.T. Bate, D.L. Carter and J.S. Wrobel: Proc. 10th Int. Conf. Phys. Semiconductors, Cambridge, Massachusetts, 1970 (the US Atomic Energy Commission, 1970) p.125.
12) See the article, H. Kawamura: Proc. 3th Int. Conf. Phys. Narrow Gap Semiconductors, Warszawa, 1977 (Elsever Scientific Pub. Co., 1978) p.7.
13) N. Kristoffel and P. Konsin: Ferroelectrics 6 (1973) 3.
14) H. Kawamura, S. Katayama, S. Takano and S. Hotta: Solid State Commun, 14 (1974) 259.
15) A. Natori: J. Phys. Soc. Japan 41 (1976) 782.
16) S. Nishi, H. Kawamura and K. Murase: phys. stat. sol.(b)7 (1980)581.
17) K.L.I. Kobayashi, Y. Kato, Y. Katayama and K.F. Komatsubara: Phys. Rev. Letters 37 (1976) 772.
18) W. Jantsch and A. Lopez-Otero: Proc. 13th Int. Conf. Phys. Semiconductors, Rome, 1976 (Tipografia Marves, Rome, 1976) p.487.
19) D.K. Hohnke, H. Holloway and S. Kaiser: J. Phys. Chem. Solids 33 (1972) 2053.
20) K. Murase, S. Sugai, S. Takaoka and S. Katayama: Proc. 13th Int. Conf. Phys. Semiconductors, Rome, 1976 (Tripografia Marves, Rome, 1976) p.305.
21) S. Takaoka and K. Murase: Phys. Rev. B20 (1979) 2823.
22) S. Katayama: Solid State Commun. 19 (1976) 381.
23) K. Murase, S. Sugai, T. Higuchi, S. Takaoka, T. Fukunaga and H. Kawamura: Proc. 14th Int. Conf. Phys. Semiconductors, Edinburgh, 1978 (The Institute Physics, Bristol and London, 1979) p.437.
24) K. Murase and S. Sugai: Solid State Commun. 32 (1979) 89.
25) Y. Onodera: Solid State Commun. 11 (1972) 1397.
26) D. Schiferl: Phys. Rev. B10 (1974) 3316.
27) P.B. Littlewood: J. Phys. C. Solid State Phys. 12 (1979) 4441.
28) S. Katayama and H. Kawamura: Solid State Commun. 21 (1977) 521.
29) H. Tanaka and A. Morita: J. Phys. Soc. Japan 46 (1979) 530.
30) S.V. Vlachos, A.P. Lambros and N.A. Economou: Solid State Commun. 19 (1976) 759.
31) S. Nishi, H. Kawamura and K. Murase: phys. stat. sol.(b)97 (1980) 581.
32) S. Katayama and K. Murase: Detailed theoretical description in this section will be published in Solid State Commun. (1980).
33) See the article, S. Sugai, K. Murase, T. Tsuchihira and H. Kawamura: J. Phys. Soc. Japan 47 (1979) 539.
34) D.L. Mitchell and R.F. Wallis: Phys. Rev. 151 (1966) 581.
35) H. Kawamura, S. Nishikawa and K. Murase: Proc. Int. Conf. on Appl. High Mag. Field in Semiconductors, Oxford (1978) p.170.
36) Okazaki: J. Phys. Soc. Japan 13 (1958) 1151.
37) H.R. Chandrasekhar and U. Zwick: Solid State Commun. 18 (1976) 1509.